Hydration of roman cements used for architectural restoration

C. Gosselin 1, K.L. Scrivener 1, S.B. Feldman 1

1 Laboratory of Construction Materials, Swiss Federal Technological Institute (EPFL), Lausanne, Switzerland, christophe.gosselin@epfl.ch,

Abstract Roman cement was extensively used to decorate facades during the nineteenth and beginning of twentieth Century. The interest of this material has been revisited recently in the field of conservation of architectural cultural heritage. This article gives preliminary results on the characterization of the raw materials and main reactive phases (using XRD, SEM, selective dissolution and isothermal calorimetry) of a roman cement recently produced from the Lilienfeld marlstone (Austria), in comparison with a commercial roman cement (from Vicat, France). The mineralogical composition of the two cements strongly differs according to the presence of sulphate minerals in the marlstone and the temperature of calcination. Isothermal calorimetry and in-situ XRD carried out on cement paste allow the identification of the AFm and AFt type phases as early age hydration products responsible of the flash setting typical to roman cements. The composition rich in alumina and the crystallinity of dicalcium silicates strongly differs in the Lilienfeld cement and influence their reactivity at the later ages.

1 Introduction

Patented in England by James Parker in 1796, roman cement was extensively used in civil engineering structures [1-3] before the invention and development of Portland cement. From the first half of the 19th century, roman cement was also used as binder for stone repair mortars and façade decoration of historical buildings all over Europe [4-6]. Since the last decade, the properties and durability of historical roman cement mortars and their compatibility with stone substrates have been demonstrated by many studies [4,7-9]. The main advantages of roman cements for stone restoration can be summarized as followed: low energy consumption resulting from low calcination temperatures (800-1100°C), durability even in highly polluted environment (urban exposure and aggressive solutions),
compatibility with historical building materials (aesthetical, chemical and transfers properties), and versatility of mortar formulations and applications techniques.

Roman cement is produced from raw marlstone rather than from a mixture of different source materials as for traditional cements (ordinary Portland cements, calcium aluminate cements, calcium sulfo-aluminate cements, belites cements…). Furthermore no gypsum is added during the grinding process to regulate the workability of fresh roman cement mortars. The raw marlstones have a wide range of chemical composition and are calcined at temperatures where sintering and melting would not occur (800-1100 °C). The “clinker” is then finely ground and usually no further product was added. According to the literature [8], it was difficult to control the composition of roman cements due to the various compositions of marlstone calcined with heterogeneous process in shaft kilns. Vicat (France) was a major company producing roman cement throughout the last two centuries and remains the only producer in Europe. Vicat Prompt cement, used alone or mixed with hydraulic lime, provides technical solutions for historical masonry repair [10,11]. The use of roman cement has been recently revisited in the frame of Rocem project [5] which aimed at investigating historic roman cement mortars to provide compatibility criteria for repair mortars [4], to select appropriate raw materials and optimize the calcination process in laboratory and pilot scale kilns [12-14]. Based on Rocem project, the new Rocare project aims at making roman cement as a compatible and sustainable product as alternative solution to available products (lime, hydraulic lime and commercial roman cements) and adapted to local needs of restoration market in Europe. This necessitates the fundamental understandings of the mineralogical development during the calcination process and the subsequent hydration reactions once mixed with water, aggregates and chemical admixtures. This article presents new results on the characterization of two different roman cements, a commercial cement (Vicat prompt cement) and a roman cement produced in the frame of Rocem project (2003-2006) resulting from the calcination of the Lilienfeld (Austria) marlstone in a pilot scale rotary kiln (920°C for 300 min), as reported in [15]. The hydration was studied from the first minutes up to three months. The main challenge of this study is the characterization of reactive amorphous phases resulting from the calcination of marlstone at low temperatures. Combined techniques for anhydrous cement characterization (selective dissolution, XRD, EDS mapping) allow the discrimination of intermixed and non crystalline phases responsible for the workability and long term performances specific to these cements.

Cementitious notation:
C- CaO , S- SiO2 , A- Al2O3 , C- CO2 , S- SO3 , H- H2O
2 Materials and methods

The oxide composition of the Lilienfeld and Vicat cements is given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lilienfeld</td>
<td>30.08</td>
<td>8.97</td>
<td>44.42</td>
<td>3.81</td>
<td>2.44</td>
<td>0.13</td>
<td>1.81</td>
<td>0.38</td>
<td>7.79</td>
<td></td>
</tr>
<tr>
<td>Vicat</td>
<td>18.70</td>
<td>7.51</td>
<td>54.8</td>
<td>3.35</td>
<td>3.90</td>
<td>3.36</td>
<td>1.08</td>
<td>0.29</td>
<td>6.97</td>
<td></td>
</tr>
</tbody>
</table>

The characterization of the cement reactants used selective dissolution methods according to the works of Stutzman et al [16]. The Salicylic Acid/Methanol Extraction (SAM) dissolves alite C₃S, belite C₂S, and free lime. The KOH/sugar solution dissolves the interstitial phases of aluminate and ferrite leaving a residue of silicates and minor phases.

Isothermal calorimetry is a technique to study the kinetics (heat flow is expressed in J.h⁻¹.g⁻¹ of cement) and the total heat (J.g⁻¹ of cement) generated by exothermic reactions occurring in controlled conditions. Five to ten grams of fresh cement paste were cast in a glass vial placed in the calorimeter (TAM Air calorimeter and thermostat 3114/3236 from Thermometric). In-situ mixing experiments were done using a specific device equipped with paddle, allowing the measurement of heat flow from the very start of the reaction [17].

The cement paste was prepared by adding water to cement (mass ratio W/C of 0.65) and mixed with a paddle mixer for 1 minute at 1100 rpm. The fresh cement paste was cast in plastic vial, demoulded after 24 h and cured in de-ionized water. A slice of specimen was cut for each test time. The hydration of the cement pastes was stopped by solvent exchange. The paste slices were cut and immersed in isopropyl alcohol for 6 days and then dried in desiccators.

XRD was carried out with an X’Pert Pro PANalytical diffractometer (Cu tube, λ=1.54 Å). The crystalline phase identification in anhydrous cements and cement paste used the powder method (after 100 micron sieving).

Scanning Electron Microscopy (SEM, Philips Quanta 200) was used to study the microstructure of anhydrous cement powder. Pelletized raw cement and cement pastes were impregnated with epoxy resin and polished to obtain cross sections. The microanalysis of phases was done with Energy Dispersive Spectroscopy (EDS, Bruker AXS Quantax). Quantitative elemental mapping was performed using ultra-fast spectral imaging acquisition for 15 min. The Esprit software (from Synergie® PGT) allows the acquisition of images with a simultaneous spectral accumulation in a database for each pixel. The set of acquired images were then treated to normalize the intensity of each chemical element with respect to its quantity determined by accumulated EDS spectra.
Finally the atomic Ca/Si and Al/Si ratios were calculated from the intensity of quantitative images (using routines developed with Matlab) and mapped inside the most representative grains of the respective cements.

3 Results

3.1 Characterization of the anhydrous roman cements

3.1.1 XRD and selective dissolution

Fig. 1 shows the XRD patterns of the Lilienfeld and Vicat cements before and after selective dissolution. The main crystalline phases present in the Lilienfeld cement originate from the incompletely calcined marlstone, e.g. quartz and calcite in relatively high amounts and albite and muscovite as secondary phases from clayey fraction. Other crystalline phases result from the calcination of the minerals in the temperature range 800-900°C. Among these phases, the diffraction peaks related to calcium silicates $\beta$ or $\alpha'$-\(\text{C}_2\text{S}\) show a relatively low degree of crystallinity in the 31-34°2θ range, compared to the well crystalline $\beta$-\(\text{C}_2\text{S}\) present in Vicat cement (Fig. 1). Secondary phases are identified as Portlandite, CH, presumably from pre-hydration of free lime. After extraction of the silicates phases by the SAM method, the XRD pattern reveals small amounts of gehlenite \(\text{C}_2\text{AS}\) and a calcium silicate carbonate, tilleyite \(\text{C}_3\text{S}_2.2\text{C}\), occurring as a natural mineral whose formation has not been reported during the manufacture of cements [18], in contrast to spurrite \((\text{C}_2\text{S})_2.\text{C}\), a carbonated form of \(\text{C}_2\text{S}\) [19] identified as traces in the Lilienfeld cement but in greater amounts in Vicat cement. One interesting result is in the strong similarity of the XRD patterns before and after the KOH/sucrose dissolution. The overlap of these two patterns indicates that the Lilienfeld cement contains no significant crystalline aluminate reactants. These results were already reported in [20].

The mineralogy of Vicat cement differs strongly from that of the Lilienfeld one and is composed of a wider range of silicates and aluminates reactants. Due to higher temperature of calcination (up to 1200°C), the crystallization of $\beta$ or $\alpha'$-\(\text{C}_2\text{S}\) is enhanced, as illustrated by the diffraction peaks in the 31-34°20 range and much less quartz remains compared to the Lilienfeld cement. The selective dissolution methods seem more suitable to the Vicat cement to discriminate the different phases. The main aluminates phases, identified after SAM dissolution,
are $\text{C}_12\text{A}_7$, $\text{C}_3\text{A}$, $\text{C}_4\text{AF}$ and $\text{C}_4\text{A}_3\text{S}$ and the main silicates phases identified after KOH/sucrose dissolution, are $\beta$ or $\alpha'$-$\text{C}_2\text{S}$ and spurrite $(\text{C}_2\text{S})_2\text{C}$.

Traces of calcium sulphate $\text{C}_3\text{S}$ were also identified in the XRD pattern of the raw Vicat cement. Compared to the Lilienfeld cement, the Vicat cement contains higher amounts of sulphate (Table 1) crystallized under the form of anhydrite $\text{C}_3\text{S}$ and ye'elimite $\text{C}_4\text{A}_3\text{S}$ which both contribute to significant changes in the hydration products (Fig. 8). The presence of calcium sulphate $\text{C}_3\text{S}$ can be explained by the release of sulphur from the weathered sedimentary pyrites included in the limestone grains, as illustrated in Fig. 5. Another source of sulphur is seldom observed in the cement grains under the pattern of calcium monosulphide CaS. This phase plausibly originates from the reaction between free lime or calcite and gaseous sulphide under local reducing conditions of calcination.
3.1.2 SEM and EDS-mapping analyses of the Lilienfeld cement

Polished cross-sections of pelletized Lilienfeld cement powder were prepared prior to SEM examinations illustrated in Fig. 2. The morphology and composition of the nodules appear to be uneven in the sample, but some general features can be identified. As already suggested by XRD, many quartz and calcite grains remain in the nodules, surrounded by a reactive phase appearing whiter grey in BSE mode. This phase presumably results from the diffusion of calcium and silicate ions during the calcination process of marlstone. However the EDS mapping (Fig. 3) suggests that alumina is systematically present in significant amounts in this phase which is consequently referred to as C-A-S reactant in this paper. Fig. 3 shows the EDS mapping on a nodule containing quartz, calcite and K-feldspar (KAlSi₃O₈ as endmember) grains surrounded by the C-A-S reactant. The elemental analysis gives a Ca/Si ratio evenly distributed in the grain and close to 1. K-feldspar is source of silica and alumina which changes the Al/Si ratio ranging 0.2-0.4 in this specific grain. The non stoichiometric composition of this phase can explain the difficulty to relate the diffraction peaks in the 31-34°2θ range to actual β or α’-C₃S.

From Fig. 2, it is noteworthy that the morphology of cement grains remains unchanged after selective dissolution methods. First, the intragranular porosity, already observed in the raw cement, does not increase significantly after. Furthermore, SAM and KOH/sucrose dissolution do not affect the C-A-S phase surrounding quartz and calcite.
Fig. 2 Microstructure of the Lilienfeld cement grains (left: raw cement – middle: after SAM dissolution – right: after KOH/sucrose dissolution)

Fig. 3 EDS mapping of the raw Lilienfeld cement

3.1.3 SEM and EDS-mapping analyses of the Vicat cement

In contrast with the Lilienfeld cement, the Vicat cement is manufactured at higher temperature and consequently better crystallized and discriminated phases are observed in Fig. 4. A typical grain is composed of C$_2$S grains surrounded by a solid solution of C$_3$A, C$_4$A$_3$$\beta$ and C$_4$AF. Some clusters of periclase MgO, resulting from the decomposition of dolomitic materials, usually appear as dark
areas in BSE mode. As already mentioned from the XRD results, little quartz remains in the cement and some porous nodules resulting from incomplete calcination are seldom seen. The morphology and composition of these porous nodules (bottom left image in Fig. 4) are comparable to those present in the Lilienfeld cement (Fig. 2). The XRD results on samples after selective dissolution are confirmed by BSE images (Fig. 4) in which the rounded $\text{C}_2\text{S}$ grains are removed by SAM solution and $\text{C}_3\text{A}$ and $\text{C}_4\text{AF}$ are dissolved after KOH/sucrose dissolution.

The EDS images for the Vicat cement (Fig. 5) show the suitability of the technique to map the silicate and the aluminate phases inside the most representative grains. Contrary to the Lilienfeld cement (Fig. 3), the $\text{C}_2\text{S}$ grains (blue in Fig. 5) have a stoichiometric Ca/Si ratio of 2 and are well differentiated from the aluminate phases ($\text{C}_3\text{A}$, $\text{C}_4\text{A}_3\overline{\text{S}}$, and $\text{C}_4\text{AF}$) illustrated in red according to the arbitrary scale bar related to the Al/Si ratio.

![Fig. 4 Microstructure of the Vicat cement grains (left: raw cement – middle: after SAM dissolution – right: after KOH/sucrose dissolution)]
3.2 **Hydration of roman cements**

3.2.1 **20°C isothermal calorimetry**

Fig. 7 shows the heat generation during the hydration of the Vicat and the Lilienfeld cements at very early age (with in-situ and ex-situ mixing). The rapid hydration of both cements is characterized by a single heat flow peak with comparable acceleration rate and intensity. For both systems, the initial heat flow peak corresponds to the dissolution of reactive phases and both the precipitation of hydration products.

The identification of crystalline hydration products was studied by in-situ XRD analysis for the first 15 hours. From the beginning of hydration, there are very different phase assemblages in the two cements. While ettringite $\text{C}_6\text{A}_2\text{S}_3\text{H}_32$ and hemicarboaluminate $\text{C}_4\text{A}_3\text{C}_0\text{.}5\text{H}_{12}$ both precipitate from the first minutes of hydration in the Vicat cement, the first phase identified in the Lilienfeld cement is $\text{C}_4\text{A}_3\text{C}_0\text{.}5\text{H}_{12}$. This phase dissolves after 5 hours hydration and reacts with carbonate ions from the pore solution to precipitate monocarboaluminate $\text{C}_4\text{A}_3\text{C}_0\text{.}5\text{H}_{11}$, which predominates after 24 hours (Fig. 8).
Regardless of the nature of hydration products, the reaction levels off after 8 to 10 minutes of hydration for the two systems. This age also corresponds to the end of the workable time of the cement pastes. At later ages, the right graph (low Y-axis scale) shows significant discrepancies in the calorimetric response between the systems. In the Vicat cement, a very sharp peak is observed from 18 hours with a maximum after 36 hours. According to XRD (Fig. 8), this peak would correspond to the precipitation of monocalciumaluminate $\text{C}_4\text{A}_2\text{C}_3\text{H}_11$. In the Lilienfeld cement, a much smaller and broader peak is seen from 2-3 days of hydration which extends over several days, and would match with the hydration of C-A-S phase as suggested by XRD (Fig. 8). The total heat curves show that the rapid formation of $\text{C}_4\text{A}_2\text{C}_3\text{H}_11$ contributes to the higher heat generated by the Vicat cement. However, the hydration rate of the C-A-S phase is greater in the Lilienfeld cement in comparison to the slow hydration of well-crystallized C2S in the Vicat cement.

**Fig. 7** Heat flow and total heat during early age and long term hydration of the Lilienfeld and the Vicat cements
3.2.2 XRD analysis of hydrated cement pastes

Fig. 8 shows the XRD patterns of cement paste cured for 90 days under water. In the Lilienfeld cement, C₄ÅCH₁₁ predominates after 24 h but with a relatively broad diffraction peak which could indicate a solid solution with initial hemicarboaluminate C₄ÅC₀.₅H₁₂, as already suggested by [20]. After 90 days, the hydration of the C₂S and the C-A-S phase seems well advanced but no crystalline hydration products were identified. In the Vicat cement, the ettringite originally formed and hemicarboaluminate C₄ÅC₀.₅H₁₂ remain stable for 90 days. The precipitation of monocarboaluminate C₄ÅCH₁₁ is initiated after 24 h and levels off after 28 days of curing under water. Compared to the C-A-S reactant in the Lilienfeld cement, very little C₂S reacts before 28 days. The hydration of C₂S is well advanced after 90 days and leads to the precipitation of calcium hydroxide CH co-precipitating with amorphous calcium silicate hydrates C-S-H.

4 Conclusions

This paper compares the mineralogy and hydration of two types of roman cements used for historical masonry. Due to the differences in the raw materials and the calcination process, the Lilienfeld and Vicat cements have different mineralogy and hydration mechanisms. These two cements rapidly hydrate and
require retardation admixture for practical applications. The higher calcination temperature in the Vicat cement leads to the formation of crystallized belites, partly carbonated to form spurrite at high CO₂ partial pressure in the shaft kiln, which are relatively low reactivity phases. The presence of sulphates (pyrites) in the raw marlstone leads to formation of calcium sulphate and ye’elimite which rapidly hydrate to ettringite. After a few minutes, the sulphate concentration rapidly becomes undersaturated with respect to ettringite precipitation and the calcium aluminates hydrate to hemicarboaluminate. This phase is unstable in presence of calcite and monocarboaluminate slowly precipitates during curing under water.

During the calcination of the Lilienfeld marlstone, incomplete crystallization of calcium silicates occurs within nodules containing significant amounts of calcite and quartz. A few grains of stoichiometric C₂S are formed and were locally observed in a rim around the quartz grains. Remaining clay materials provide aluminate ions leading to the formation a non stoichiometric C-A-S phase. The XRD and SEM results after selective dissolution indicate that silicate and aluminate are intimately linked in this poorly crystalline C-A-S phase. The diffusion of ions seems to be incomplete under these conditions of calcination to form purely crystallized C₂S. The XRD pattern of this C-A-S phase would suggest a disordered structure for which the reactivity is enhanced compared to the crystallized β and α'-C₂S. However crystalline hydrates as calcium hydroxide, which is the usual product of C₂S hydration, were not detected after 90 days of curing.

5 Acknowledgements

This study was initiated in the frame of Rocare project (EU 226898) financially supported by the European Commission (FP7-ENV-2008-1 program).

6 References


