PROPOSAL FOR A USEFUL METHODOLOGY FOR THE
STUDY OF ANCIENT MORTARS

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Abstract

In the framework of a preliminary study concerning the restoration of a historic building, the knowledge of the environment, the structure and materials of the concerned building is very useful, indeed necessary, in order to propose an adapted and durable restoration works.

Regarding the particular, although very broad point of mortars, a lot of problems have appeared. It is possible to quote some of them: knowledge of ancient local techniques, refection of mortars or coated, grouting necessary to the reinforcement of a masonry, treatment of recent unsuitable repair mortars.

All these themes impose to know, among others, the nature of mortars in masonry. It is therefore important to base the analysis on two main indissociable axes: the determination of the qualitative and/or quantitative composition of the material studied (chemistry, mineralogy, distribution of porosity) and the study of its state of conservation. The complementary proposed analyses, and nevertheless necessary for the use of a specific software of calculation of mortars and concrete composition (Calcul Minéraux LCPC), can be the following:

- chemical analysis of the acid soluble fraction,
- thermogravimetric analysis allowing the determination of water content of hydrates and the carbonates content,
- examination under optical microscope by reflected light or X rays diffraction analysis in order to identify the binder phase of mortars,
• examination under optical microscope by transmitted light allowing the petrographical identification of the sand,
• examination under scanning electron microscope coupled to an X ray microanalysis allowing the characterisation of the materials microstructure and the detection of anomalies or signs of physical and chemical degradations.

In this paper, each of these techniques will be briefly detailed; their complementarity and their applications will be presented. Real case studies will validate the methodology: the study of mortars of the church of Penmarc’h, and the study of the Mont Saint Michel masonry (Boucle tower).

1. Introduction

The study of mortars which constitute ancient buildings, whether used as binding, filling or coating offer many advantages: improving the knowledge of ancient and/or local techniques, preparation of some restoration materials matching the original ones and formulation of grouts fitting to characteristics of the studied masonry.

The presented methodology proposes an approach which contains two complementary steps: one is the determination of the qualitative mineralogical composition through a "microstructure approach", and the other one, if necessary, is the physico-chemical analysis allowing the use of a specific software well suited to mortar or concrete characterisation: the Calcul Minéraux LCPC.

Two case studies will allow to give examples of real results: they concern a rubble mortar from the church of Penmarc’h in Brittany, and the filling mortars of the masonry of one of the towers of the Mont Saint Michel in Normandy.

2. Methodology

2.1 Advantage of the preliminary qualitative mineralogical approach

The acquired experience in the ancient mortars characterisation has shown that the knowledge of the nature of the studied material before carrying out its quantitative mineralogical analysis is of prime necessity. As a matter of fact this first stage enables us to determine the need or not of further of analysis. Several interesting methods can be used, their choice dependent on the aim of the study. These methods as well as their main applications are as follows [1]:

• visual examination by the naked eye and through a magnifying lens. This preliminary examination is necessary prior to any microstructure study; it guides in a relevant manner the samplings as well as the choice of the other investigations that are to be realised.
• X-ray diffraction analysis: this method is very useful for the determination of the mineralogical nature of the binder (particularly in the case of sulphate binder) and for the detection of the crystallised alteration products.
• optical microscopy in transmitted polarised light: mineralogical and petrographical identification of sand.
• optical microscopy in reflected light: identification of hydraulic binders, of anhydrous clinker particles, and of the mineral admixtures.
• scanning electron microscopy (SEM): characterisation of carbonates and hydrates (nature, form, structure ...) of the matrix, identification of the alteration phases.
• energy dispersive X ray microanalysis coupled with SEM: local qualitative and quantitative elementary composition of the phases under observation.

2.2 "Calcul Minéraux" contribution- Quantitative determination
The microstructural approach which allows identification of the components of the mortar does not enable us to determine the relative amounts of the various components. The best way is to connect the chemical analysis of the major components after attack of the soluble part of the mortar by diluted acid (HNO₃ 1:50) with the thermogravimetric analysis [2, 3].

The chemical analysis of the soluble fraction corresponds to the oxides contents of the binder and to the carbonates present in the mortar stemming from the sand and/or from the carbonation of the matrix. As for the insoluble residue, it corresponds to the siliceous fraction of the sand, and with some possible other components whose dissolution is not complete: pozzolana, fly ash, slag etc.

The thermogravimetric analysis allows for the measurement of the various types of waters (free water, bounded water etc) and of the carbonates by measuring the corresponding loss of carbon dioxide (CO₂).

These analysis and measurements are required for the calculation of the mortar mineralogical composition by the mean of the "Calcul Minéraux LCPC". This computer calculation was initially conceived for modern concretes, but is well suited to the analysis of ancient mortar [4]. For this calculation an assumption is made on the chemical composition of the initial binder which is used as a basis for the calculation of the ratios (oxides from the mortar analysis) / (oxides of the binder). The main oxides used are SiO₂, Al₂O₃, CaO, MgO and SO₃. Through a series of iterations, it is possible to approximate the composition of the initial binder, and to capture the mineralogical species recognised through the mineralogical analysis. Thus, the mineralogical composition can be obtained by connecting the global calculation and a calculation with a previously selected pilot-oxide.
As for any normative calculation, the balance of the oxides "consumption" allows a final appraisal of the result achieved. However there is such a large "freedom" as far as the computer operations are concerned, that it is necessary to have a thorough scientific knowledge of the binders chemistry in order to carry out and validate the calculation.

Thus, using the data obtained from the chemical and thermogravimetric analysis as well as from the microscopic observations, the computerised calculation enables the determination of the mineralogical composition of the mortars expressed in mass percentage. The main points that are brought out are:

- a good approach of the initial binder composition.
- an evaluation of the binder amount in the mortar.
- the nature and the amount of the various types of aggregates (dolomite, calcite, quartz and silicate (insoluble residue).
- the nature and the amount of the newly formed mineral species (ettringite, chloroaluminates, halite, ...).

The case studies in chapter 3 will complete and illustrate this theoretical presentation.

2.3 Limits of the method and supplementary analysis

In two main cases the proposed method may not be enough to determine the precise composition of the mortar:

- presence of some insoluble or partly soluble compounds in the initial binder. In fact, some pozzolanic materials (fly ash, slag, clinker ...) that might belong to the binding phase, can contain a high non-reactive fraction which is insoluble in the conditions of the attack. In order to obtain a better result, a chemical analysis of the residue may be carried out and the mineralogical composition determined and taken into account in the global result.
- The most common case is the one of mortars or concretes whose matrix is highly carbonated. On that account, distinction between the calcite of the calcareous sand and the newly formed calcite becomes impossible via the method referred to in this paper. Some authors try to combine thermogravimetric (TGA) and the differential thermal analysis (DTA) to make this sharp distinction [5]. Nevertheless another supplementary method seems to be more convenient: some recent works have shown that the stable isotope contents (\(^{13}\text{C}\) and \(^{18}\text{O}\)) of the natural carbonates are very different from the ones of the carbonates formed within mortars and concretes (fig. 1). Quantitative acidic extraction of the CO\(_2\) which is transferred in an isotope ions collector, quantification of the various isotopes by mean of mass spectrometry allows us to quantify and distinguish the newly formed carbonates and the carbonates from the sand [6, 7].
Fig. 1: Isotopic ratio distribution within various carbonates [7].

3. Model of investigation

3.1 The jointing mortar of Penmarc’h’s church (Brittany)

This particular study relates to a binding mortar quarried from the granite masonry of the Saint Nonna church in Penmarc’h, which is located in Brittany and dates back to the XVth century. The purpose of this study was to estimate its state of preservation and to come close to a similar formula in order to restore the building [8].

3.1.1 Examination and qualitative analysis.

The light tinted mortar does not appear degraded to the naked eye and seems rather cohesive. It is mainly constituted by siliceous sand, the granularity of which does not exceed five millimetres.

The X-ray diffraction analysis of the fraction corresponding mainly to the binder shows a prevailing presence of calcite as well as a considerable amount of calcium chloro-aluminate 3CaO.Al2O3.CaCl2.10H2O, and a lesser amount of ettringite 3CaO.Al2O3.3CaSO4.32H2O.

The microscopic observations show that, apart from the carbonated zone, the paste is formed by calcium silicate hydrates (C-S-H) assembling and hydrated calcium silico-aluminates joined up with some needle-shaped or prismatic ettringite crystals. In spite of the fact that they form a highly porous material, the hydrates do not show any significant

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domain I: marine sedimentary limestones (fillers and aggregates)
domain II: limestone laid from continental waters
domain III: carbonates precipitated from cements in open air and fresh water
domain IV: carbonate precipitated from cements in water of Paris region
domain V: archaeological cement samples from Mycenes
domain VI: from Knossos
domain VII: from Champlieu (France)
domain VIII: modern cements of various origin with and without limestone fillers
sign of degradation; at the very most, they display some slight signs of partial dissolution.

One peculiarity of this mortar is the presence of a rather high amount of calcium chloroaluminates of massive crystal form (fig. 2), and located in the macro-porous zones of the matrix where they appear to be well included.

![Calcium chloroaluminate crystals](image)

Fig. 2: calcium chloroaluminate crystals (1) located in the capillary porosity of the mortar (SEM)

### 3.1.2 Chemical analysis and calculations

The result of the chemical analysis is transcribed in the chart below.

The chemical analysis indicates that the soluble fraction is mainly constituted of CaO, SiO₂ and Al₂O₃; it can correspond to the composition of a hydraulic binder. The insoluble residue corresponding to the siliceous sand is close to 50% in weight of the product mass.

The mortar binder is mainly composed of carbonates and calcium silico-aluminates hydrates which would proceed from a pozzolanic reaction between clay and lime. However, the fact that it also contains many carbonated zones coming from a transformation of the calcium hydroxide Ca(OH)₂, clearly indicates that there was an excess of lime in this mixture.

The differential thermal analysis underlines the presence of hydrated calcium silicates C-S-H, hydrated calcium aluminates and probably of a kaolinic type clay.
Table 1: Analysis of the Penmarc’h mortar (weight %)

<table>
<thead>
<tr>
<th>Species</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>6.99</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.30</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.27</td>
</tr>
<tr>
<td>CaO</td>
<td>18.91</td>
</tr>
<tr>
<td>MgO</td>
<td>0.34</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.39</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.40</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.28</td>
</tr>
<tr>
<td>Cl</td>
<td>0.39</td>
</tr>
<tr>
<td>Siliceous insoluble</td>
<td>48.70</td>
</tr>
<tr>
<td>Loss of ignition</td>
<td>20.85</td>
</tr>
<tr>
<td>Total</td>
<td>99.84</td>
</tr>
<tr>
<td>Free water</td>
<td>7.00</td>
</tr>
<tr>
<td>Bound water</td>
<td>8.10</td>
</tr>
<tr>
<td>CO₂</td>
<td>5.75</td>
</tr>
</tbody>
</table>

The calculation gives a binder proportion of about 25% in weight and confirms that one of the characteristics of this binder is its strong hydraulicity. It would correspond to the composition of a modern cement containing some siliceous addition.

The products observed are rich in sulphates and chlorides (ettringite and chloro-aluminates) but they do not seem to be linked to a possible degradation of the mortar. Their good integration into the material tends to show that they are of primary formation: they could originate from the mixing water where some seawater could have been present.

The calculation has also allowed quantification of those species which are not usually found in lime mortars: calcium chloro-aluminates (3 %) and ettringite (1.5 %).

### 3.2 The filling mortar of the Boucle Tower (Mont Saint Michel)

The purpose of this study was to determine the nature and the quantity of alteration products through the characterisation of several samples of filling mortar from the granitic masonry of one of the tower of the Mont Saint Michel, prior to carrying out some structural reinforcements; the alteration products have to be taken into account before choosing and preparing the injection grouts that were to be used.
3.2.1 Examinations and qualitative analysis.
The various tests and analysis have shown that:

- all the mortars examined have the same texture and qualitative composition. Their microstructural examination shows lightly micro-porous sand-paste interfaces, and a matrix having medium cohesion,
- this matrix is mainly composed of locally highly micro-porous calcium silicate hydrates (C-S-H) which often show clear signs of dissolution. Many crystals of secondary ettringite crystals, that have habits that vary from prismatic to massive (fig. 3), are associated with the C-S-H. Ettringite seems locally linked to a pattern of micro-cracks,
- in the most porous zones, some highly developed hexagonal calcium chloro-aluminate crystals have been observed. Also, the elementary analysis of the matrix almost always shows a chlorine pick, the intensity of which can vary,
- in some specific zones some (C,M)-S-H hydrates coming from the transformation of the C-S-H through a substitution of calcium for magnesium from the sea water, are found.

Fig. 3: Massive ettringite of an expansive type (1) within the matrix of one of the mortars (SEM).

3.2.2 Chemical analysis and calculations.
The results of the physico-chemical analysis carried out on two of these mortars are given in table 2.
Table 2: Analysis of the Boucle tower mortars (weight %)

<table>
<thead>
<tr>
<th></th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>2.47</td>
<td>2.28</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.71</td>
<td>0.71</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.37</td>
<td>0.54</td>
</tr>
<tr>
<td>CaO</td>
<td>11.57</td>
<td>9.41</td>
</tr>
<tr>
<td>MgO</td>
<td>7.81</td>
<td>0.59</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.15</td>
<td>0.16</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.08</td>
<td>0.12</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.78</td>
<td>0.16</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.14</td>
<td>0.18</td>
</tr>
<tr>
<td>Siliceous insoluble</td>
<td>61.68</td>
<td>76.93</td>
</tr>
<tr>
<td>Loss of ignition</td>
<td>13.80</td>
<td>8.50</td>
</tr>
<tr>
<td>Total</td>
<td>99.58</td>
<td>99.60</td>
</tr>
<tr>
<td>Free water</td>
<td>0.5</td>
<td>1.4</td>
</tr>
<tr>
<td>Bound water</td>
<td>6.2</td>
<td>4.2</td>
</tr>
<tr>
<td>CO₂</td>
<td>7.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The above results confirm that both of the mortars are constituted of a qualitatively identical binder (see the silica and the alumina contents). They also show that one of the samples displays higher sulphate and magnesium contents. These results reflect the strong influence of the marine environment. In both mortars the chloride contents are rather high.

The results of the calculations are given in a simplified form in table 3.

Table 3: computed calculation of the Mont Saint Michel mortars composition

<table>
<thead>
<tr>
<th></th>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siliceous aggregates in weight %</td>
<td>61.6</td>
<td>76.9</td>
</tr>
<tr>
<td>Carbonates in weight %</td>
<td>13.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Anhydric binder in weight %</td>
<td>14.25</td>
<td>13.15</td>
</tr>
</tbody>
</table>

These mortars correspond to either a pure hydraulic binder or to pozzolanic type binder, which show some significant alteration signs from physico-chemical origin: dissolution of many of the initial hydrates, Mg-Ca substitution inducing a cohesion loss of the matrix, neoformation of mineral species which could be expansive and coming from the reaction of chloride ions and sulphates from the sea water with the original aluminates of the mortar's binder.
4. Synthesis and conclusions

A methodology for the assessment of ancient mortars was presented. Its application to two case studies has shown that it has allowed:

- determination of the composition of a specific mortar containing a lime and kaolin binder, which points out an ancient knowledge of such pozzolanic mixtures. From a geographical point of view, the assumption that seawater was used as mixing water is also possible; in addition, the chloride ions might have promoted the hydration reactions. Besides, the reconstitution of this mortar in laboratory has confirmed that this mixture resulted in the development of the identified mineral phases [8],
- precise determination of the nature and of the state of alteration of the filling mortar. This has made possible an adaptation of the restoration grouts. Thus the filling grouts have been made with a binder matching the environment: possible and necessary hydraulic nature, low tri-calcium aluminate content in order to reduce the risks of combination with the existing sulphate ions...

Both cases constitute two very specific examples, and do only concern hydraulic or pozzolanic binding materials. The methodology has also been used for other types of mortars, whether they be plaster, slaked lime, natural cement, Portland cements or binders mixtures. The following examples could be mentioned: the pharaoh period plaster mortars [9], the Ptolemy period lime - plaster Egyptian coatings, the slaked lime mortars of the Poitiers and Amiens’ cathedrals [10], the natural cement of the Coignet concrete dating back to the end of the XIXth century [11], and the concretes and mortars of this century as a whole [12].

Such analyses are also useful for the characterisation of present-day mortars showing some early disorders. This type of study may for instance enable us to check if the requirements related to a restoration site have been followed.

Finally, it is important to bring up again that this method can be used partially or taken as a whole, depending on the frame of the study and of the aim of the characterisation of the concerned material. But the need for a previous qualitative petrographical and mineralogical study remains essential; in a majority of cases this study even proves itself sufficient.

5. References