Analysis of Mortars (to include historic mortars) by Differential Thermal Analysis.

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Abstract.

In the world of Historic Buildings Repair, the philosophy governing the specification of repair mortars is like for like. Unless there are very good reasons for not doing so, the repair mortar should accurately replicate the existing. In this way, a good colour and texture match is achieved. Performance characteristics, and perhaps more importantly the ageing, weathering and decay processes and patterns, are appropriate both aesthetically and technically.

Proper, accurate, analysis of existing mortars, plasters, and renders is therefore crucial when considering the selection of materials to be used and the method to be adopted when conserving or repairing historic buildings.

Rose of Jericho has been analysing mortars, principally historic mortars, for many years and for the last three using DTA in addition to chemical and microscopic testing. DTA is a sophisticated analytical technique which records the temperatures at which the components of a mortar decompose. It is particularly good at distinguishing between calcium compounds, and is therefore used primarily to determine binder type. It is a recognised technique but it has only recently been recognised as useful in the analysis of historic mortars.

1. INTRODUCTION.

Rose of Jericho has been analysing ancient mortar samples from all types of old buildings for ten years with many of the samples being taken from buildings of national importance.

Rose of Jericho has a stand alone analytical department but also specialises in the manufacture and supply of all types of lime mortars, plasters, renders and paints to the conservation industry. The philosophy governing the specification of repair materials is like for like; that is, to match the existing as closely as possible, and this doctrine is generally appropriate. Materials are matched technically; this is not a simple colour and
Clearly, it is essential to identify confidently the components of the existing materials in order to be able to design a suitable matching mix.

The buildings from which samples have been analysed include:

- Historic Royal Palaces
- Scottish Castles
- Cathedrals
- Churches
- Tithe barns
- Roman Villas
- Bridges
- Locks
- Aqueducts

The samples are of all types: interior, exterior, surface, core, underground, underwater.

In many instances there are reasonably accurate records of construction and repair phases and contextual information of this nature is always helpful.

Because of the historic importance of these buildings often only small samples can be taken and insufficient numbers tested in order to obtain a reasonably confident overall assessment of the existing mortar. The standard tests for mortar examinations are to carry out chemical tests primarily to determine the proportions or percentage of:

- Calcium oxide (CaO)
- Soluble silica (SiO$_2$)
- Insoluble residue

However these tests are prone to errors and will generally only identify the presence of a hydraulic binder in a fresh or recently placed mortar. With ancient mortars the early reaction products change and age, and therefore the interpretation becomes more difficult without resorting to further testing for confirmation purposes. To improve the information on the testing of these ancient mortars Rose of Jericho has for the last few years routinely carried out Differential Thermal Analysis in addition to chemical analysis and microscopic examination.

Differential Thermal Analysis can be carried out on very small samples and, depending upon the constituents remaining after ageing, can identify if any calcium silicate hydrates,
sulphates or complex hydrates remain. Over 300 samples have been tested in this manner and from the results and accumulated data collected a number of interesting features are emerging. This paper highlights the broad trends and discusses where further analysis such as SEM or XRD could assist.

The results and discussions are limited to those mortars defined as ancient.

2. REASONS FOR ANALYSIS OF HISTORIC MORTARS.

The major reason is to identify the components that were used as binding or cementing constituents of ancient mortar.

Pre 1900 these could have been:

- Slaked or hydrated lime.
- Hydraulic or semi-hydraulic lime.
- Roman and natural cements.
- Aspdin or early Portland cement.
- Gypsum.
- Clay, mud, and earth.
- Combinations of the above.

In addition to these materials there is the possibility of reactive aggregates and pozzolanic materials. Simple chemical analysis alone cannot specifically identify the original materials or constituents.

Hydrated lime will react with carbon dioxide to produce calcium carbonate and this will proceed in a moist environment and only extremely slowly in dry air or under water. The other compounds of lime or cements consisting mainly of silicates or aluminates can be classified as natural semi-hydraulic lime, natural or Roman cements, Portland or early cement, and alumina cement. It is these that develop strength under water.

Ageing of hydraulic limes and early cement mortars over 100 years will result in the breakdown of the early hydration products to form silica gel, tobermorite, calcium carbonate and inert aggregate. In the right environment the hydrates may be very durable and still exist.

Therefore Rose of Jericho carries out mortar testing for these reasons:
Accurately analyse the mortar to determine the constituents.
- Examine which are of historical significance and worthy of matching.
- To enable the specification of a mix design for those worthy of matching.
- To examine the relationship between the complexity of ancient mortars and their durability.
- To establish reasons for failure or poor performance. (Present day mortars only.)
- To gain an understanding of the materials available historically and their performance characteristics and to establish a data information library.

3. THERMAL ANALYSIS

Thermal Analysis has been employed by geologists, ceramicists, and scientists for many years as a rapid analytical tool for determination and identification of clays and other materials, phase transitions and phase diagrams.

It has been widely used in many sectors of the building materials industry:
- to determine the hydrate structure of Portland cements.
- to determine free hydrated lime.
- to measure the degree of pozzolanic activity.
- to determine the extent of conversion in high alumina cement.

According to the International Confederation for Thermal Analysis the following conventions are used:
- Thermogravimetry (TG) is used for measuring weight loss.
- Derivative Thermogravimetry (DTG) for determining the rate of weight loss.
- Differential Thermal Analysis (DTA) is used to measure the temperature difference between sample and standard.
- Differential Scanning Calorimetry (DSC) has become more widely used as it measures both the temperature and the enthalpy of a transition or the heat of reaction or decomposition.

In accurate convention terms the work reported in this paper is DSC, but since no quantification of the energy from the thermograms have been made, DTA is used.
In this method a sample is heated at a linear heating rate in a selected atmosphere (usually air). The differential thermogram shows the difference in temperature between the sample under test and a thermally inert reference material, alumina. The enthalpy of a transition or the heat of reaction whether endothermic or exothermic is measured as a fraction of temperature. For mortars the maximum temperature was limited to 900°C in order to measure the decomposition of calcium carbonate.

4. THERMAL DECOMPOSITION DATA

The main hydrates found in hydraulic cements will be those associated with the reaction between water and the calcium aluminates and silicates. The presence of sulphate will also produce a series of hydrates.

The complexities of the decomposition of the hydrates of calcium silicates and aluminates have been studied extensively. The temperature range where water is lost during the heating regime in the DTA test samples for the various hydrate structures that may be present in the sample are given in the table below.

Table 1. Thermal Decomposition Data for Hydrated Compounds.

<table>
<thead>
<tr>
<th>COMPOUND NAME</th>
<th>FORMULA</th>
<th>TEMPERATURE °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium Silicate Hydrates</td>
<td>CSH Type 1 &amp; 2</td>
<td>95 – 120</td>
</tr>
<tr>
<td>Ettringite</td>
<td>C_4ASH_{12}</td>
<td>125 – 135</td>
</tr>
<tr>
<td>Monosulphate</td>
<td>C_6ASH_{32}</td>
<td>185 – 195</td>
</tr>
<tr>
<td>Syngenite</td>
<td>K_2CaS_2H</td>
<td>265 – 275</td>
</tr>
<tr>
<td>Hydrated Lime</td>
<td>CH</td>
<td>495 - 550</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>CaCO_3</td>
<td>850 – 1000</td>
</tr>
<tr>
<td>Gypsum (dihydrate)</td>
<td>CSH_2</td>
<td>160 – 185 (two peaks)</td>
</tr>
<tr>
<td>Calcium Sulphate Hemihydrate</td>
<td>CSH</td>
<td>185</td>
</tr>
<tr>
<td>Calcium Aluminates</td>
<td>CAH_{10}</td>
<td>110 – 130</td>
</tr>
<tr>
<td></td>
<td>C_2AH_8</td>
<td>175 – 185</td>
</tr>
<tr>
<td></td>
<td>C_3AH_6</td>
<td>280 – 320</td>
</tr>
</tbody>
</table>

S = SO_3
The above examples are not a complete list of the possible constituents that could be found to exist in new and ancient mortars. There are many more crystalline forms of calcium silicate hydrates as well as there being a whole series of partially carbonated hydrates.

Ettringite loses a considerable amount of its crystal water on drying as do monosulphates. The monosulphoaluminate $C_4ASH_{12}$, $C_4AH_{13}$ and $C_2AH_8$ are all structurally related and lose water on drying. Therefore old samples, or samples that have had an arid environment regime during their history, or even if heat was generated during core sampling, will not produce the same intensity peaks as cured fresh samples. This must be taken into account when interpreting DTA results.

5. **DTA CHARACTERISTICS OF ANCIENT MORTARS**

From the DTA results of historic mortars there are several distinct features that regularly occur, and can be classified into four broad groups although this does not mean that all mortars with a similar profile are the same. Mortars from different sources have their own unique profile, albeit that some of the differences are trivial. These groups could be further sub-divided into additional groups.

The broad classifications are:

**Group 1**

The main distinguishing feature in the thermograms of mortars that fall within this group is that there is no evidence of endothermic reactions seen in the temperature range between 80°C to 300°C.

This is clearly evident in the 3 examples shown in Figures 1.1 to 1.3:

**Figure 1.1** 1642, The Cage, Lyme Park.

**Figure 1.2** 1657, Mells Manor.

**Figure 1.3** 1639, Burgate Manor.

The calcium and soluble silica test results for these examples are:
The DTA shows that calcium silicate hydrates or complex sulphate salts are absent but significant soluble silica results could suggest some evidence of hydraulicity during the history of these mortars. Microscopic examination of 1642 and 1657 showed that ash and clay are present, and this is shown by the exothermic activity in the thermograms.

These profiles include non-hydraulic and aged (possibly weakly hydraulic) lime mortars.

**Group 2**

In this group there is clear evidence of a single endothermic peak in the region between 90°C and 200°C. From the data it is clear that the single peak occurs either around 100°C to 125°C or between 150°C to 180°C. Typical examples are shown in Figures 2.1 to 2.3:

**Figure 2.1** 1611, Woodchester Mansion.

**Figure 2.2** 1718, St. Peter's, Exton.

**Figure 2.3** 1607, Queen Anne's Gate.

The chemical test results for these examples are:

<table>
<thead>
<tr>
<th>TEST</th>
<th>Figure 2.1</th>
<th>Figure 2.2</th>
<th>Figure 2.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Woodchester</td>
<td>St Peters</td>
<td>Queen Anne</td>
</tr>
<tr>
<td>CaO %</td>
<td>43.9</td>
<td>28.0</td>
<td>35.0</td>
</tr>
<tr>
<td>SiO₂ %</td>
<td>2.0</td>
<td>6.5</td>
<td>1.2</td>
</tr>
<tr>
<td>SO₃ %</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

The peak observed at 100°C to 130°C is only seen in samples with a significant water and
soluble silica content. The evidence therefore suggests that this could be CSH but it is also possible that there is a high clay content and this is physically bound water within the clay.

Likewise there is a clear correlation between the endothermic peak seen between 150°C and 180°C and the concentration of sulphate measured in the sample. It is not clear whether this peak is the hemihydrate salt of calcium, a more complex salt, or a poorly defined gypsum peak.

Comparing the data with Group 1 mortars, it is clear that for accurate interpretation of the results, further analysis such as XRD or SEM may resolve the identities of the compounds detected.

Group 3

Group 3 differs from Group 2 in that there is evidence of a more complex hydrate structure as two or more endothermic peaks are observed in the temperature range between 100°C and 300°C. These peaks indicate the remnants of compounds of hydrated calcium silicates and aluminates, but these are not distinguished in this broad classification. This can be seen in the examples in Figures 3.1 to 3.3.

Figure 3.1 1594, Greys Bridge.

Figure 3.2 1605, Winchester Castle Hill.

Figure 3.3 1725, Warminster Bedding.

The chemical test results for these examples are:

<table>
<thead>
<tr>
<th>TEST</th>
<th>Figure 3.1</th>
<th>Figure 3.2</th>
<th>Figure 3.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Greys Bridge</td>
<td>Winchester</td>
<td>Warminster</td>
</tr>
<tr>
<td>CaO</td>
<td>8.5</td>
<td>19.2</td>
<td>17.1</td>
</tr>
<tr>
<td>SiO₂</td>
<td>3.7</td>
<td>6.4</td>
<td>2.9</td>
</tr>
</tbody>
</table>

The mortars that fall within this category include Portland and early cements, natural cements and hydraulic limes, and lime/pozzolana mortars.
The sample from Greys Bridge (Figure 3.1) is a typical aged Portland cement, the sample from Winchester Castle Hill (Figure 3.2) is of a type known as 'Roman Cement', and the Warminster sample (Figure 3.3) is a lime mortar containing brick dust which has clearly reacted.

**Group 4.**

The mortars that are categorised in this Group clearly contain calcium sulphate dihydrate or a proportion of calcium hemi/dihydrate sulphate in the samples. The concentration of sulphate ($SO_3$) ranges from <1.0% to 45%. These are gypsum mortars and gypsum:lime hybrids.

This can be seen in the 3 examples in Figures 4.1 to 4.3:

**Figure 4.1 1676, Somerset House.**

**Figure 4.2 1717, Stoneleigh Abbey.**

**Figure 4.3 1626, Hampton Court Palace.**

The chemical test results for these examples are:

<table>
<thead>
<tr>
<th>TEST</th>
<th>Figure 4.1</th>
<th>Figure 4.2</th>
<th>Figure 4.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Somerset House</td>
<td>Stoneleigh Abbey</td>
<td>Hampton Court</td>
</tr>
<tr>
<td>CaO %</td>
<td>22.0</td>
<td>50.0</td>
<td>23.8</td>
</tr>
<tr>
<td>SiO$_2$%</td>
<td>0.7</td>
<td>0.2</td>
<td>1.4</td>
</tr>
<tr>
<td>SO$_3$%</td>
<td>32.4</td>
<td>25.8</td>
<td>3.6</td>
</tr>
</tbody>
</table>

This group is distinguished from Group 2 in that there is a distinct double endothermic peak around 160°C to 185°C that can be assigned to the calcium sulphate dihydrate/hemihydrate.

The samples that contain less than 5% sulphate ($SO_3$) are of more academic interest, and often indicate the results of polluted environments.

**6. CASE STUDY**
The Vyne, Basingstoke. (National Trust)

A sample of external base-coat render from the portico to The Vyne was analysed in order to ascertain the constituents of the binder. The records showed that this material is a relatively recent mortar with an age of c. 40 years. The DTA result (Figure 6.1) clearly indicated this to be in a sub-division of Group 3, and the presence of calcium silicates, calcium hydroxide, a small proportion of fine calcium carbonate and quartz are clearly identified.

Further analysis of this sample was undertaken using SEM with EDAX, with the intention of identifying alite (C3S) and belite (C2S).

SEM analysis positively identified calcium silicate hydrates and partially hydrated belite (C2S). Calcium hydroxide, calcium carbonate and feldspar were also identified. No evidence of alite (C3S) was seen in the sample and this supports the documentation received that the mortar was at least 30 years old.

It is interesting to note that lime still exists in this sample after 40 years.

Fig 6.1 The Vyne, Portico Render.

7. OVERALL ASSESSMENT OF DATA

1. The results from the testing of ancient mortar samples using DTA, chemical and microscopic examination have clearly identified the extreme caution needed in identifying the existing components, let alone the original constituents.

2. In some samples chemical analysis identified a significant soluble silica content but DTA did not find a trace of any hydrates.

3. In other samples with similar chemical composition there was clear evidence of decomposition of silicate or aluminate hydrates and for the more important structures it would be of great interest to analyse these by SEM, XRD, or IR spectroscopy.

4. It is also possible to carry out thermogravimetric analysis and DTA with simultaneous evolved gas analysis.

However, any examination that measures only part of the characteristics or properties of a mortar that is related to the durability or performance of the mortar cannot provide the complete answers. Before specifying the best mix design for a repair mortar, it is essential that a good understanding of the physical, mechanical and surface morphology is obtained for the mortar requirements in relation to the environment and the building structure. Only with this information can one specify with confidence the proportioning
ratios of the recommended components that could be attributed to the mix design formulation.

APPENDIX 1.

Buildings from which samples have been tested include:

- British Museum
- Dore Abbey
- Edinburgh Castle
- Hampton Court Palace
- Kew Palace
- Many Ancient Monuments
- Many Scottish castles
- Midford Aqueduct
- Mottisfont
- Rochester Medieval Walls
- Royal William Yard
- Somerset House
- Stoneleigh Abbey
- The Cage, Lyme Park
- The Vyne
- Tower of London
- Windsor Castle
- Woodchester Mansion