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Thermal analytical investigation of unaltered $Ca(OH)_2$ in dated mortars and plasters

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Abstract

The presence of unaltered relics of hydrates of calcium and magnesium in dated plasters and mortars are investigated by thermal analysis, X-ray powder diffraction, and by hydration of dated specimens after incremental heat treatment in a muffle furnace. The results are compared with the literature. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The presence of $Ca(OH)_2$ in dated mortars and plasters is discussed in the literature by Lea [3], Marchese [5], Marchese and Garzillo [4], and in two papers by Newton and Sharp [7,8].

Marchese and Garzillo [4] report unaltered relics of $Ca(OH)_2$ and $Mg(OH)_2$ in Italian mortars. They offer the following observation. A specimen was subjected to both differential thermal analysis (DTA) and thermogravimetric analysis (TGA). A determination of the Ca^{++} content was made by chemical analysis of the specimen. A content corresponding to 69.5% $CaCO_3$ conflicted with a content of 64% $CaCO_3$, determined by TGA analysis. The difference in values can be seen as 5.5% $CaCO_3$ and 4.1% $Ca(OH)_2$, respectively. They theorize that this represents the amount of $Ca(OH)_2$ unaltered due to the carbonation mechanism suggested by Lea [3]. Marchese and Garzillo quote Gourdin and Kingery, who studied specimens of mortar by scanning electron microscopy (SEM) report the following:

> The SEM examination of the fracture surfaces shows a compact texture at low magnification. At higher magnification, the texture is one of roundish grains of different sizes and the fracture is intergranular in character. Some porosity is visible and the voids are quite irregular in their shape and volume. The unchanged $Ca(OH)_2$ must be located at the centre of the grains of carbonate where the CO_2 from the atmosphere is unable to penetrate.

Marchese and Garzillo attribute their inability to find the characteristic peaks for $Ca(OH)_2$ in X-ray powder diffraction analysis to a state of low crystallinity in the $Ca(OH)_2$, postulated in an earlier report [5]. The present study indicates that fractions of minerals of <5% might have been obscured by background noise in earlier XRD diffractograms [5]. They further state that chemical analysis of the same sample indicates a $MgCO_3$ content of 27.8%, an amount >23% shown by TGA, adjusted to 21% if allowance is made for unaltered $Ca(OH)_2$. They theorize that an amount of $Mg(OH)_2$ equal to 4.7% also remained

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unchanged and is represented by a weight loss of 1.9% (310–420°C) on the TGA curve.

The findings of Marchese [5], and Marchese and Garzillo [4] are in contrast to those of Newton and Sharp [8]. They report that the 'critical' endotherm of 510°C attributed by Marchese and Garzillo to $Ca(OH)_2$ was only found in plasters of dolomitic origin. Further, they report substantial loss of mass at 500°C (based on TGA) in plasters containing significant amounts of magnesium. Sharp and Newton, and Marchese and Garzillo have observed unexpected reactions during thermoanalytical studies of dated plasters and mortars, particularly those of dolomitic origin.

It is clear that mortars and plasters produced from dolomitic limestones require close examination, inasmuch as endotherms in the range of 500°C have been reported. The proper identification of minerals in mortars of dolomitic origin is further complicated by the possibility of solid-state reactions occurring during the thermolanalytical study of specimens [8]. They report that in a mixture of $Ca(OH)_2$ and $MgCO_3$ heated by the DTA method the expected endotherm for $MgCO_3$ was missing, further, an unexpected endotherm for $CaCO_3$ was found. They suggest a solid-state reaction based on the following equation:

$$Ca(OH)_2 + MgCO_3 \rightarrow Mg(OH)_2 + CaCO_3$$

The proposed reaction would remove the $MgCO_3$ (magnesite). Sharp has proposed the following possibility. A solid-state reaction occurred at a temperature greater than that associated with the dehydroxylation of $Mg(OH)_2$ (520° and 380°C, respectively). The resulting products of the reaction produced unexpected endotherms. The first at 520°C can be attributed to the late reaction for the newly formed $Mg(OH)_2$. The same solid-phase reaction produced $CaCO_3$, thereby shifting the decarbonation reaction to a higher temperature.

The above observation caused Sharp and Newton, to conclude that unaltered $Ca(OH)_2$ (other than trace amounts) have not been found in either the plasters in their study, or in the Italian mortars as reported by Marchese [5], and by Marchese and Garzillo [4].

2. Carbonation of medieval mortars

The literature contains several statements concerning the carbonation of lime in dated structures. The author most quoted on the subject is Lea [3] who stated:

> Mortar taken from buildings many hundreds of years old, if uninjured, is found to consist of mainly calcium hydroxide, only the external portions having been converted to carbonate.

Abraham [1], who wrote that historically, medieval mortars possess slow-setting characteristics, said:

> These mortars of aerated lime set only with extreme slowness when not exposed directly to the air. In walls of medium thickness the final set can be figured in years, whereas in wall of very great thickness centuries can pass before the final set is acquired.

Other authors have referenced Lea and have drawn similar conclusions. Mark [6], wrote:

> The process (recarbonation) is slow under ordinary circumstances because the percentage of carbon dioxide in the atmosphere is low. In addition, diffusion beyond a thin surface of carbonated mortar deep into the masonry occurs at a very slow rate, if at all.

Lea's conclusions regarding recarbonation are qualified by the statement "...if uninjured...". Further, the physical condition of the mortars under consideration by Mark, or by Abraham is not discussed in their reports, further, experimental data in support of their conclusions is not reported.

The question of unaltered relics of $Ca(OH)_2$ in dated plasters and mortars addressed by Sharp and Newton [8] has prompted a reinvestigation of data concerning medieval mortars published by the present authors [2]. This previous study of dated mortars by the present authors included the following experimental method. A sample of that portion of 34 medieval mortars (previously disaggregated) passing the 200 sieve was subjected to an incremental heat treatment in a muffle furnace. The specimens were weighed at reaction temperatures observed during an earlier thermoanaytical study of prepared standards. A weight loss occurring at 450–460°C was assumed to represent the dehydroxylation of ($Ca(OH)_2$). Justification for this assumption was based on the following observations. First, no exothermic oxidation of organic material was identified during previous differential thermal analysis of the specimens under review. Second, nearly one half of the collected mortars studied by X-ray powder diffraction had a minor phase for portlandite and no evidence for the presence of magnesium carbonate ($MgCO_3$). Third, an endotherm that matches the dehydroxylation of $Ca(OH)_2$ was observed in a simultaneous TGA–DTA study of similar medieval mortars from Salisbury Cathedral (see MED.007). Fourth, in each case (for the structure under consideration), the source of building stone indicates high calcium limestone with no evidence of dolomitic limestone. The incremental heat-treatment data was used as an aid in the replication of the original mortars. The residue resulting from each specimen in the above study was stored in a desiccator for future study.

3. Simultaneous TGA/DTA analysis of hydrated residues

The analysis of aged mortars from medieval structures is facilitated by the use of thermal analytical methods. This is especially true for mortars where the decomposition of a number of phases occur. These phases include the decomposition of calcium hydroxide ($Ca(OH)_2$), calcium carbonate ($CaCO_3$), calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$) and clay minerals.

Four of the residues selected from the above study were hydrated using distilled water. After 1 h, the specimens were dried in a vacuum oven at 28.5 inches Hg and at a temperature of 30°C to remove hygroscopic water. The hydrated mortar specimens were then studied using the simultaneous TGA–DTA analysis method. The above analysis produced no endotherm for $Mg(OH)_2$. The DTA endotherms for $Ca(OH)_2$ in the hydrated residues are 117 at 460°C, 118 at 460°C, 119 at 468°C and 137 at 460°C. These endotherms were referenced against a $Ca(OH)_2$ standard of 462°C. All of the residues examined are from Salisbury Cathedral and Gloucester Cathedral. These mortars were removed during restoration work (replacement of stone) and were selected because of their soundness.

Hydration and thermal analysis of mortar residue is useful in determining total available CaO content in dated mortars. Table 1 shows the results of the analysis. Table 2 shows a comparison between the calculations for CaO in the hydrated mortar residues, the CaO from $CaCO_3$ in the collected mortars, and the total CaO in the collected mortars.

In each case, the quantities of CaO attributed to $CaCO_3$ in the collected mortar samples is less than the CaO obtained from its hydrated residue, indicating the presence of unaltered $Ca(OH)_2$ in the dated mortars (117, 118, 119, and 137). It is also noted that the total

Table 1
Results of simultaneous TGA/DTA analysis of hydrated residue

Hydrated residue no.	Weight loss percent	Onset temp. (°C)	Final temp. (°C)	CaO from hydrate	CaO from mortar
117	16.21%	411°C	466°C	50.43%	54.43%
118	9.34%	414°C	466°C	29.06%	31.15%
119	16.67%	414°C	474°C	51.86%	53.36%
137	16.48%	411°C	467°C	51.27%	53.13%

Table 2
Comparison of CaO in selected mortars

Collected mortar sample no.	CaO from hydrated residue	CaO from $CaCO_3$ collected mortar	Total CaO in collected mortar
117	50.43%	46.41%	54.43%
118	29.06%	25.93%	31.15%
119	51.86%	46.52%	53.36%
137	51.27%	44.24%	53.13%

CaO attributed to both $CaCO_3$ and unaltered $Ca(OH)_2$ in the collected mortars is greater than that indicated in the hydrated residues. A possible cause lies in the incomplete hydration of the residues prior to drying. The additional CaO in the selected hydrated residues is shown to be from 3.13 to 7.03% greater than that derived from $CaCO_3$ in the collected mortars and from 1.5 to 4.0% less than that shown for total CaO in the collected mortars. It is also noted that the total CaO value assigned to the collected mortar was based on identifying a weight loss at 600°C to the reactant $Ca(OH)_2$, whereas, a partial weight loss might have resulted from the dehydroxylation of certain clay minerals; however, endotherms were not present for those potential reactants.

4. X-ray powder diffraction parameters

The X-ray diffraction (XRD) data were collected on a SCINTAG XDS2000 diffractometer with CuK_α, γ=1.5406 Å and solid-state Ge detector cooled by liquid nitrogen. The experimental conditions were as follows: 45 kV, 40 mm, divergent beam slits 2 and 4 mm, receiving slits 1 and 0.2 mm, 2Θ=5 to 60°, continuous $\Theta:\Theta$ mode with scan rate of 2°/min and step size of 0.02° for intensity integration. The measurements were taken at room temperature, in air and at normal pressure. The data were processed using Scintag software DMS2000 ver. 2.45 on Microvax 3100 with Tektronix 4207 for graphical display. $K\alpha_2$ data have been stripped from raw intensity, background subtracted and the data smoothed using 'fast fourier filtering'. The peak data are based on esd multiplier 4.0, ripple multiplier 1.5, smoothing (three points) no standard. The search match was made against JCPDS, subfile Inorganic Minerals, user's 'periodic table': H, Ca, Mg, C, Si, O, S.

5. X-ray diffraction results: Comments

The major phase in sample 112 is portlandite (#04-0733), other phases include quartz (#33-1161), calcite (#05-586) and dolomite (#36-0424). Samples 101 and 109 have calcite (#05-586) as the major phase with a prominent diffraction pattern for portlandite (#04-0733) and quartz (#33-1161) as a third component. The major phase in samples 106 and 119 is calcite (#05-586) accompanied by quartz (#33-1161). There might be traces of hunite ($Mg_3Ca(CO_3)_4$, #14-0409) present in samples 106 and 119 (peak at 2.84 Å). Sample 138 consists mainly of calcite (#05-586) and quartz (#33-1161) at ≈1 : 1. There are two peaks around 2Θ=27 to 28° that have not been identified.

Ordinals for diffractograms:

Base line ordinal=2θ (10–60°)
Top ordinal=Angstroms (8.838–1.541 Å)
Right ordinal=Intensity (0–100%)

Mortar specimen 112 identified as a mid-nineteenth-century restoration mortar (Exeter Cathedral) is shown in Fig. 1. The mortar was not included in the complete study because of its extreme hardness and the inability to separate the component fractions of the aggregate. A sample of mortar (Med.007), ca. 14th century, from the tower at Salisbury Cathedral was examined by XRD (see Fig. 2). Computer analysis identifies calcite as the major phase with portlandite and quartz as minor phases. It can be seen from the diffractograms that crystalline phases with peaks as low as 2% intensity can be detected.

Table 3 shows the results of nine collected mortar specimens that were submitted to XRD analysis. These mortars were collected from the cathedrals of Exeter, Gloucester and Salisbury in England, and Chartres in France. Two samples represent mortars from an excavation on Rue S. Fulbert, Chartres, France, ca. 12th century.

Mortar sample 138 (Rue S. Fulbert) consists of calcite and quartz (roughly 1 : 1) and mortar Med.006 (Rue S. Fulbert) consists of calcite and quartz (roughly 2 : 1).

Mortar samples 101 and 109 (Salisbury Cathedral) have prominent patterns for portlandite and date from the 14th ca. tower and 13th ca. parapet wall, respectively. The mortar samples from Rue S. Fulbert (Med.006 and 138) were completely uncemented at the time of collection and would not be expected to contain unaltered $Ca(OH)_2$. Sample Med.005 (Chartres Cathedral) from the interior of a tower (altitude: 30 m) was poorly bonded with its aggregate. Samples 106 (Salisbury Cathedral) and 119 (Gloucester Cathedral) were well-bonded mortars. Mortar samples 101, 109 and Med.007 (Salisbury Cathedral) are all exam-

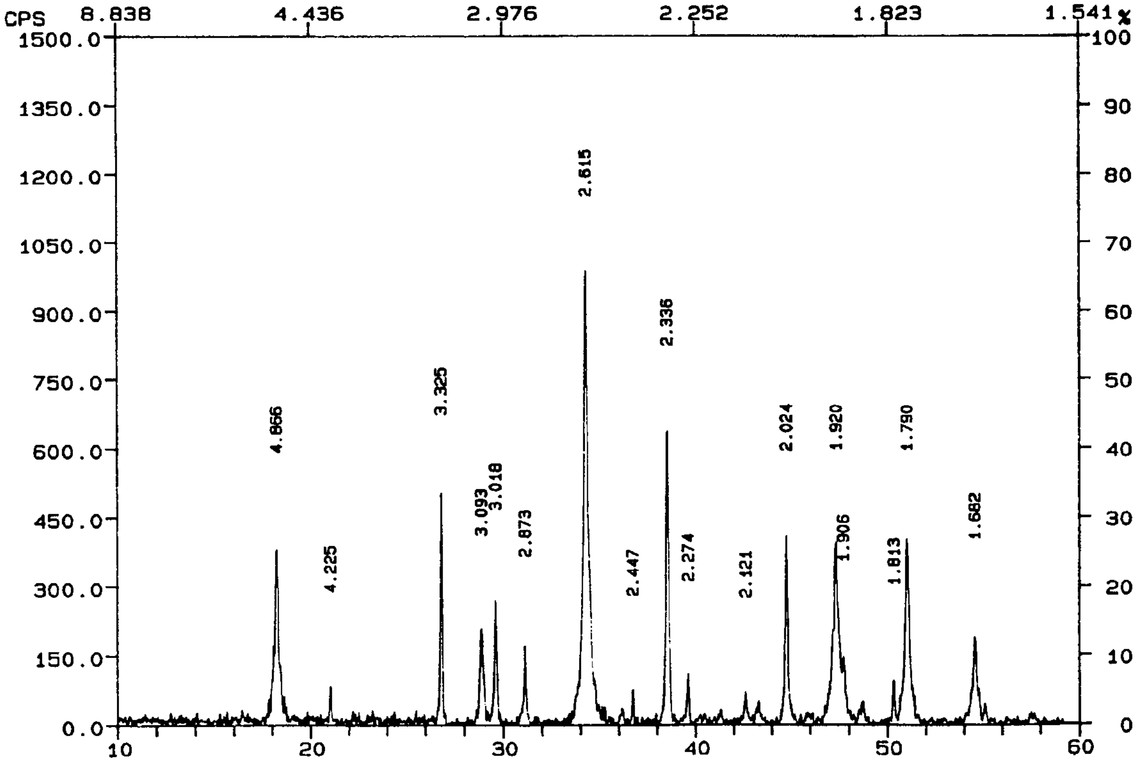

Fig. 1. X-ray data: Mortar sample no. 112.

ples of well-bonded mortars, sample Med.007 was collected from the interior of the spire tower at Salisbury. Mortar sample Med.005 (Chartres Cathedral) was collected from the interior of the northwest tower. Mortar sample Med.006 (Rue S. Fulbert) is an 11th century mortar. With the exception of mortar samples Med.005, Med.006 and Med.007 the mortars presented in the XRD study were not part of the thermal analytical study.

6. Simultaneous TGA/DTA: Referenced by XRD

Sample Med.007 was processed by simultaneous TGA/DTA and the thermogram shown in Fig. 3 was referenced against the diffraction data (see Table 3). The endotherm appearing at 460°C in the DTA curve is referenced to a weight loss of 1.364% in the TGA curve. The DTA endotherm identifies $Ca(OH)_2$ and the dehydroxylation represented by the 1.36% loss corre-

Table 3
X-ray powder diffraction data: Dated mortars

Mineral	101	106	109	112	Med.006	119	Med.005	Med.007	138
Portlandite	Prom. [d]		Prom. [d]	Maj. [a]				Min. [b]	
Calcite	Maj. [a]	Maj. [a]	Maj. [a]	Min. [b]	Maj. [a]	Maj. [a]	Maj. [a]	Maj. [a]	Maj. [a]
Quartz	Min. [b]	Min. [b]	Min. [b]		Min. [b]	Min. [b]		Min. [b]	Maj. [a]
Dolomite				Min. [b]					
Huntite		Tra. [c]				Tra. [c]	Tra. [c]		

[a] Major.
[b] Minor.
[c] Trace.
[d] Prominent.

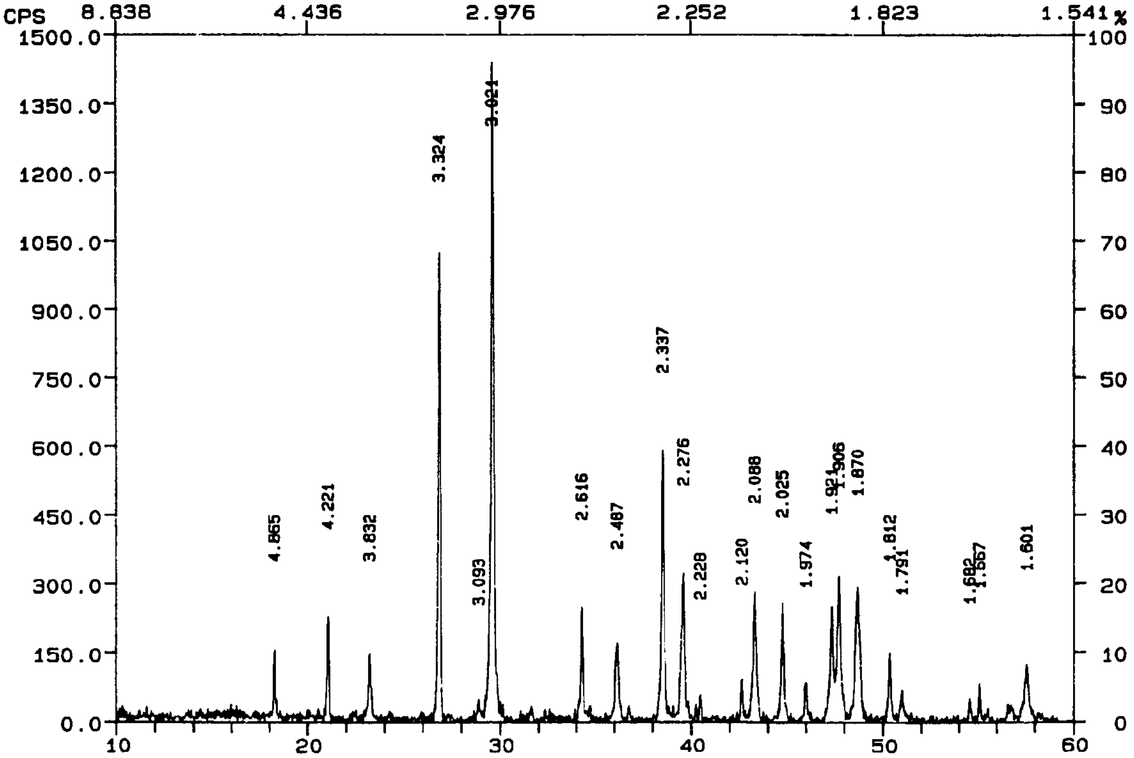

Fig. 2. X-ray data: Mortar sample no. 133.

sponds to 5.61% $Ca(OH)_2$ in the sample. There is a clear indication of the quartz transition at 573°C and the major component, $CaCO_3$, is identified by a weight loss of 18.81% (CO_2) representing 42.75% $CaCO_3$ in the sample.

Sample Med.005 shown in Fig. 4 is nearly pure calcite (86.76%) with a DTA endotherm for CO_2 at 820°C corresponding to a 38.19% weight loss in the TGA curve. The slight endotherm at 135°C results from the dehydration of gypsum.

7. Simultaneous TGA/DTA analysis of selected mortars

Figs. 5–7 show three mortars collected from the tower at Salisbury Cathedral. These mortars are similar in the respect that they all represent depths of from 10 to 20 cm from the surface (exterior) at $\approx$65 m altitude and have reached near complete carbonation. These mortars exhibit a slight weight loss beginning at 200°C. The mortars are identified as Med.001, Med.002 and Med.008, respectively. There is no indication of unaltered $Ca(OH)_2$ in these mortars, suggesting that, in contrast to the literature, dated mortars, even if uninjured, can carbonate completely.

Mortar from the interior nave of Chartres Cathedral was examined by both the DTA and the TGA method. The TGA curve produced no identifiable step for the dehydroxylation of $Ca(OH)_2$; however, the DTA curve clearly exhibited an endotherm with a peak temperature of 475°C. Relics of unaltered $Ca(OH)_2$ might be present but in such small amounts as to be unidentifiable in either XRD, or TGA.

It has been observed in the present study that thermogravimetric analysis alone will not always reveal identifiable thermal events, especially when the event is closely followed by, or overlaps a subsequent thermal event. Thermal transitions of this type can alter the onset and the return to the base line in DTA; however, trace amounts of a reactant might be better observed in DTA rather than TGA.

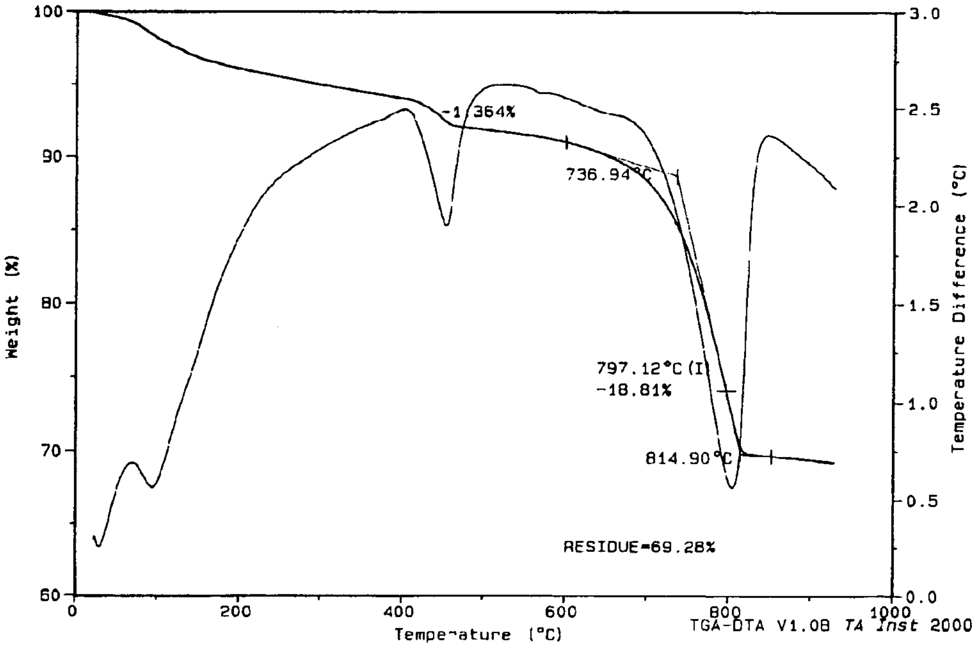

Fig. 3. Simultaneous TGA/DTA of mortar Med.007: Salisbury Cathedral.

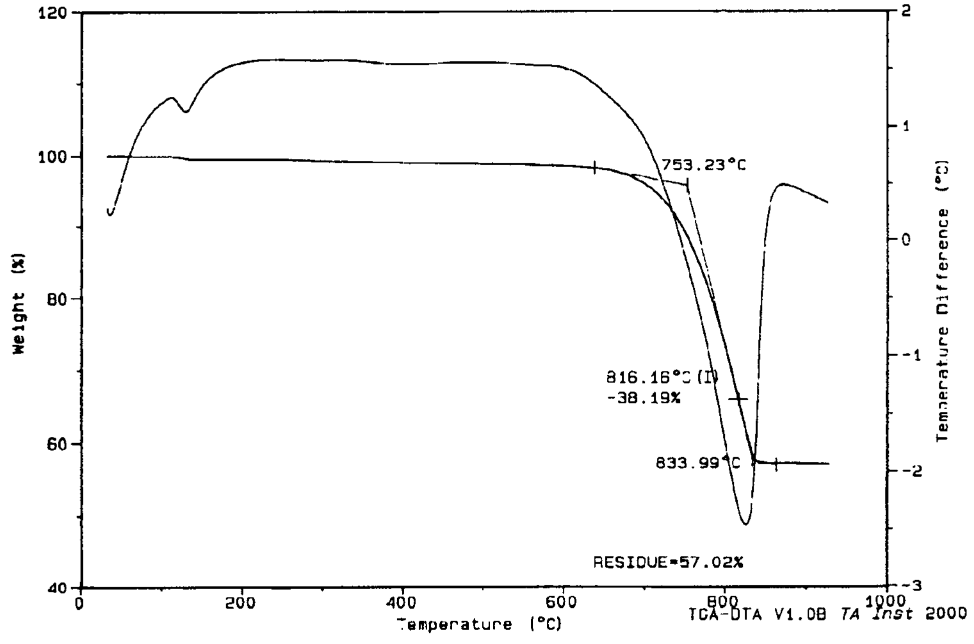

Fig. 4. Simultaneous TGA/DTA thermogram of mortar sample Med.005.

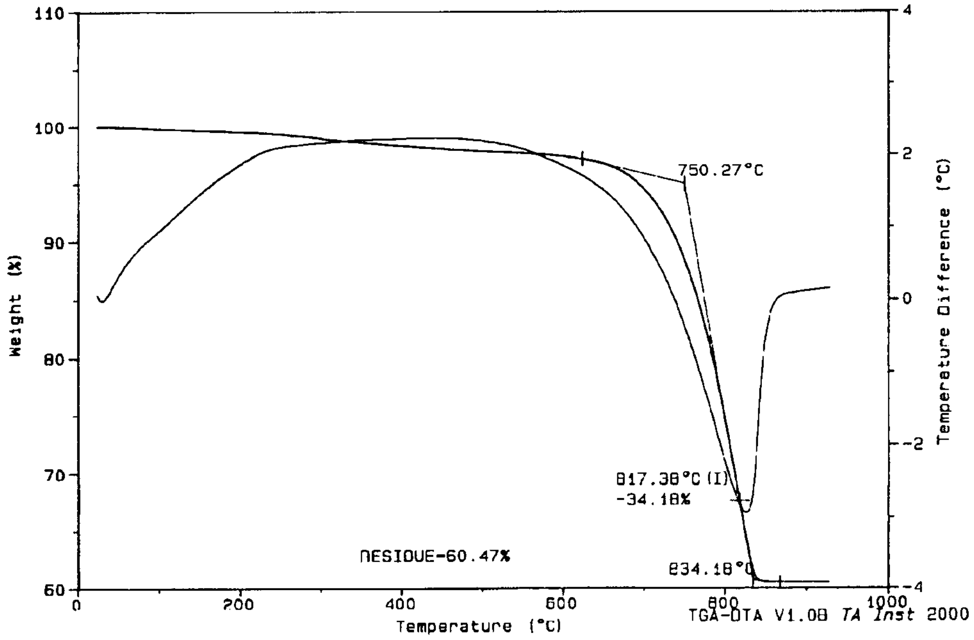

Fig. 5. Simultaneous TGA/DTA of mortar sample Med.001.

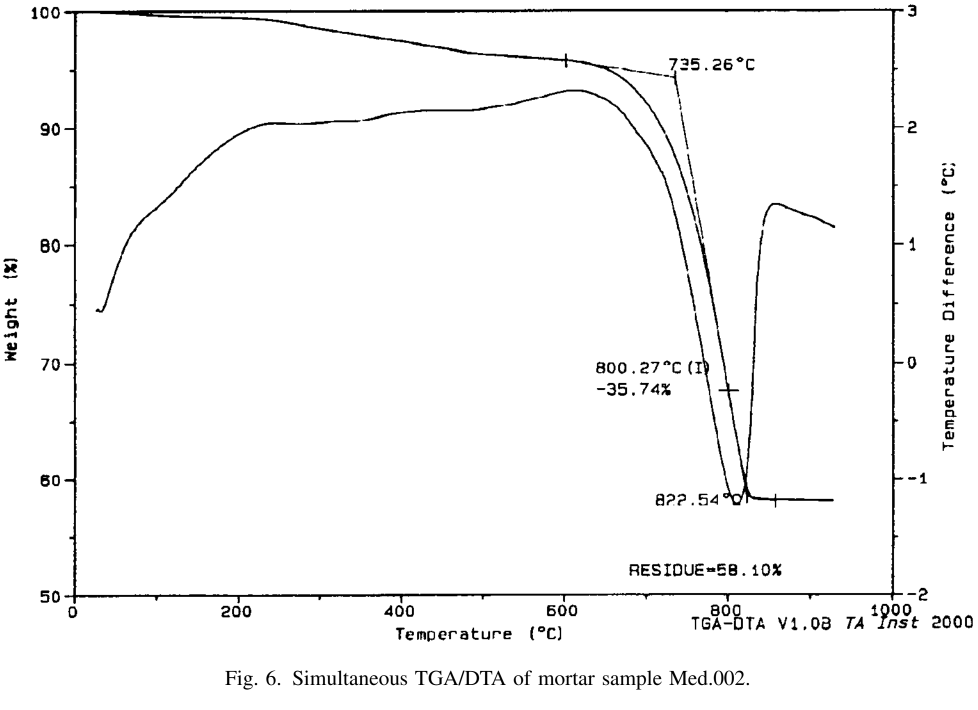

Fig. 6. Simultaneous TGA/DTA of mortar sample Med.002.

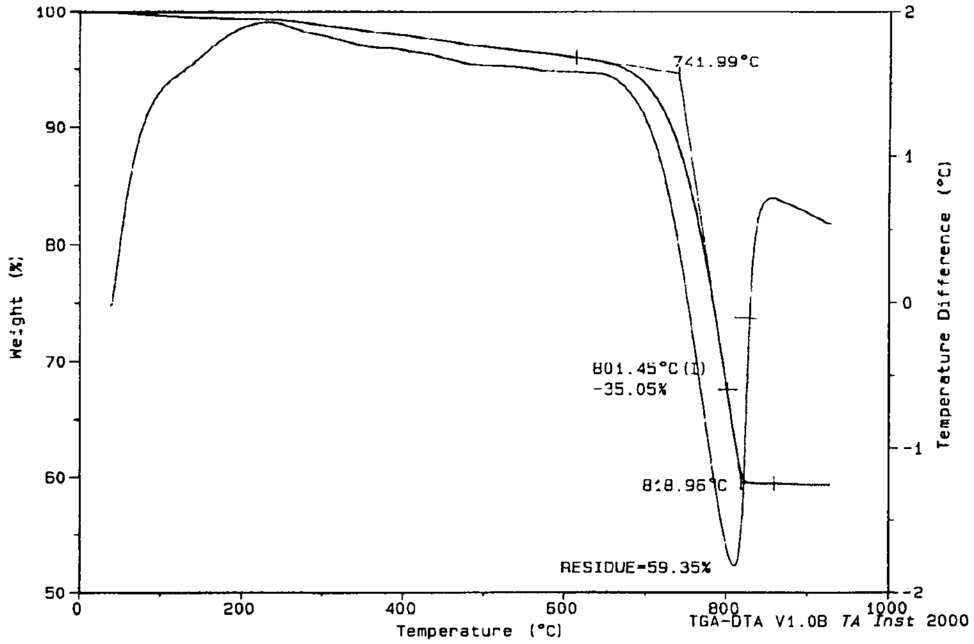

Fig. 7. Simultaneous TGA/DTA of mortar sample Med.008.

8. Simultaneous TGA/DTA analysis for carbonation in restoration mortars

Thermal analysis was carried out on four specimens of mortars currently in use at Salisbury Cathedral, Salisbury, UK. These mortars are identified as 170, 171, 172, and 173. Table 4 shows a comparison between the lime-to-sand ratio and the extent of carbonation after one year.

The slaked lime-to-sand mixtures prepared by the masons at Salisbury Cathedral have a volumetric relationship as opposed to weight. The volume of putty increases 2–3 times that of dry lime when slaked and its weight increases ≈2.5 times. The proportions customarily stated for lime putty/dry sand mortar are one part lime putty to 2.5–3 parts dry sand [6]. The Salisbury mortars range from 1–1.75 to 1–2.25 presumedly to increase the workability of the mortar. The high degree of unaltered $Ca(OH)_2$ in these mortars might be attributed to their high lime : sand ratio.

9. Carbonation in dated mortars and plasters

The present research has not included a study of plasters; however, several observations are made regarding the question of unaltered $Ca(OH)_2$ in these materials. The question of $Ca(OH)_2$ either of low crystallinity, or unaltered in dated plasters has been thoroughly examined and discussed in the literature by

Table 4
Results of simultaneous TGA/DTA analysis of restoration mortars: Salisbury cathedral

Restoration mortar sample no.	Slaked lime/dry sand ratio in mortars	Percent (Wt.) unaltered $Ca(OH)_3$ at one year	Percent (Wt.) $CaCO_3$ at one year
170	1 : 2.5	54.19%	21.45%
171	1 : 2.5	56.13%	17.04%
172	1 : 1.75	70.19%	10.40%
173	1 : 2.5	77.55%	5.77%

Sharp and Newton [7,8]. The evidence is compelling in support of their conclusions that $Ca(OH)_2$ does not exist in a state of such low crystallinity that it cannot be detected by X-ray powder diffraction and that except for trace amounts, unaltered calcium hydroxide will not be found in dated plasters. Plaster is a material that is applied in a relatively thin coating over a substrate, typically stone or wood. These coatings can vary from 1 to 4 cm or more in thickness. For any given volume of plaster the surface area is extremely large. In contrast, in dated stone structures erected primarily in compression, for any given volume of mortar the exposed surface is extremely small. Mortar beds can be 1–1.5 cm in thickness by more than 1 m in depth. The superficial area (exposed to the atmosphere) of a mortar bed plus the evidence presented in the present research accounts for detectable amounts of crystalline, unaltered $Ca(OH)_2$, in uninjured mortar beds.

10. Conclusions

Contrary to the literature, it is observed from the present study that most medieval lime mortars have reached a near total state of carbonation. The evidence presented in the present study is compelling in support of this conclusion. Mortars collected in France from the cathedrals of Chartres, Laon, Soissons, Bourges and Notre-Dame in Paris are shown to be substantially $CaCO_3$ with an occasional relic of $Ca(OH)_2$. These relics of $Ca(OH)_2$ are nearly undetectable by XRD, or TG. It is difficult to build an adequate body of evidence in support of the existence of unaltered $Ca(OH)_2$ in French mortars of the medieval period in other than trace amounts. The few cases in which an endotherm for $Ca(OH)_2$ is identified are not adequately supported by other experimental data. There are however, several examples of English mortars both medieval and Victorian, that clearly contain substantial amounts of unaltered portlandite.

The experimental data pertaining to the extent of carbonation in medieval mortars includes data obtained from XRD, TGA, DTA, simultaneous TGA/DTA and particle size distribution of the aggregate. The evidence is clear in the case of French mortars that near total carbonation has occurred. Further, oversize aggregate in most medieval French mortars analyzed in this study, coupled with low ratios of lime to aggregate result in mortars of high permeability. A high permeability factor and lime proportions of <20% in all but a few examples have resulted in complete carbonation. Though complete carbonation has occurred, the mortars are extremely friable with uncemented aggregate.

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