Thermochimica Acta, 211 (1992) 93–106
Elsevier Science Publishers B.V., Amsterdam

Thermal analysis (TA) of lime- and gypsum-based medieval mortars

J. Adams [a], W. Kneller [b], and D. Dollimore [c]

[a] *Department of Chemistry, University of Salford, Salford (UK)*
[b] *Department of Geology, University of Toledo, Toledo, OH 43606 (USA)*
[c] *Department of Chemistry, University of Toledo, Toledo, OH 43606 (USA)*

(Received 9 April 1992)

Abstract

Thermal analysis was used to investigate the composition of mortars taken from the cathedrals of Chartres, Soissons, Bourges, Paris, and Laon. In addition, mortars from structures pre-dating the thirteenth-century cathedral of Chartres were obtained from the Rue S. Fulbert archaeological site, opposite the cathedral. The literature widely reports that historical masonry is constructed with lime mortar. The present study shows that gypsum mortars were used in France at the cathedrals of Chartres and Bourges in the early thirteenth century.

INTRODUCTION

The so-called 'fat-lime' mortars of medieval France provide the basis for this study. These medieval mortars have generally been characterized as 'slow setting'. Abraham [1] 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 walls of very great thickness, centuries can pass before the final set is acquired.

The ultimate strength of lime mortars, notwithstanding consideration of the lime-to-aggregate ratio, results from the reaction between a calcareous component, calcium oxide CaO and added H_2O to produce calcium hydroxide $Ca(OH)_2$. The reaction involves the precipitation of calcium hydroxide in the form of colloidal hydroxide. Subsequent strength develops by reaction with carbon dioxide to form calcium carbonate ($CaCO_3$). Nearly all the mortars collected during two years of field work in France fit the above category. The cathedrals at Chartres and Bourges

---

Correspondence to: D. Dollimore, Department of Chemistry, University of Toledo, Toledo, OH 43606, USA.

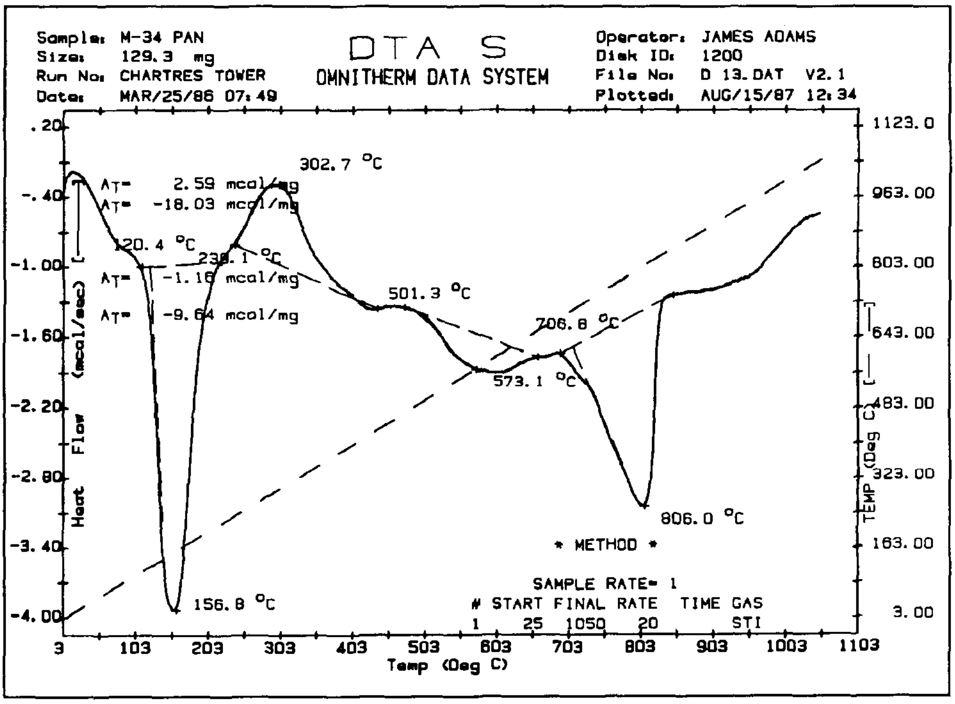


Fig. 1. DTA of gypsiferous mortar found at Chartres Cathedral.

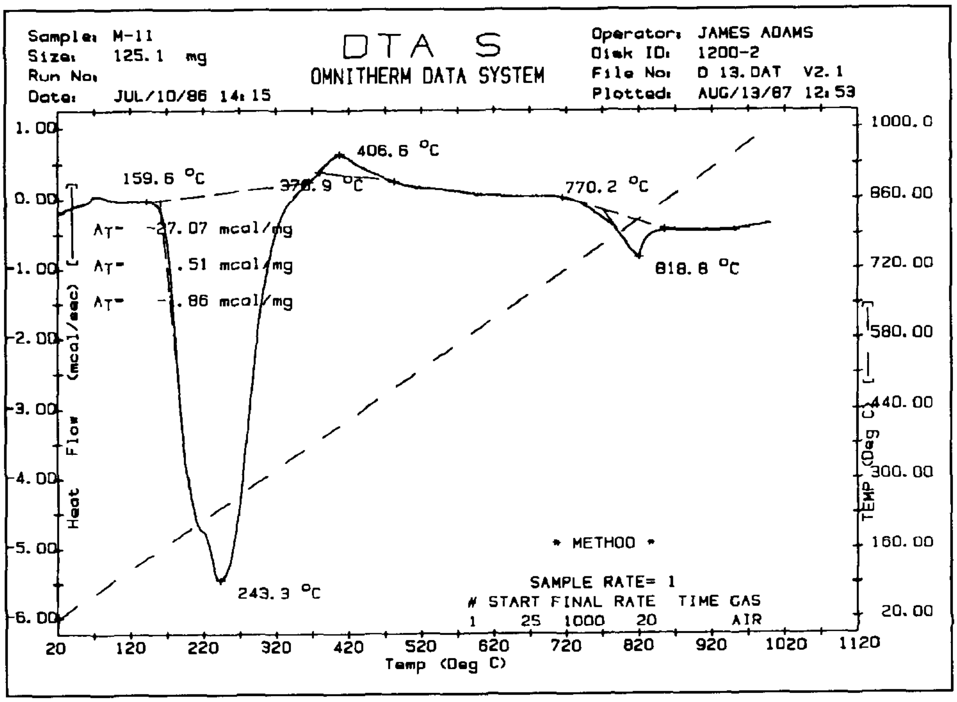


Fig. 2. DTA of gypsiferous mortar found at Bourges Cathedral.

contain examples of both lime mortars and mortars of hydrated calcium sulfate ($CaSO_4 \cdot 2H_2O$).

The literature reports that the observance of gypsum in dated structures occurs from the reaction between lime mortars and atmospheric pollution (sulfur dioxide). The present study shows that gypsum mortars were used in medieval cathedrals. Figures 1 and 2 (DTA thermograms) show gypsiferous mortars found at Chartres and Bourges that contain up to 25% gypsum. Wallace [2], writing in Chemical News in 1865, reported that mortars from the Great Pyramid contained 81.5% gypsum and 9.5% calcium carbonate. Choisy [3] confirmed these findings and placed the use of lime in Egypt during the Roman period, stating that prior to that time, gypsum was used almost exclusively. Choisy concluded that the carbonate found by Wallace was simply an impurity in the gypsum bed.

THE CHEMISTRY OF LIME MORTARS

The thermal decomposition of limestone produces CaO and CO_2. The decarbonation occurs at temperatures above 800°C. Above 800°C, depending on stone size, internal pressure and heat produce an evolution of CO_2 resulting in the formation of calcium oxide. Excessive temperature produces ‘hard burned’ lime of high shrinkage, high density, and low chemical reactivity. In contrast, lower burning temperatures result in ‘soft burned’ lime of low shrinkage, low density, high porosity, and high chemical reactivity. It is clear that the inability of the medieval lime burner to control temperature to this degree sometimes yielded poor quality lime and inconsistent properties in their mortars.

Hydration occurs through the reaction of CaO and H_2O. However, the hydration of ‘hard burned’ lime may take years at atmospheric pressure. Other factors can also retard the hydration of lime to produce $Ca(OH)_2$. Impurities can coat the oxide with a slag, resulting in low water absorption. Excessive water will mute the heat of reaction.

THE CHEMISTRY OF GYPSUM MORTARS

In its natural state, calcium sulfate dihydrate (gypsum) occurs with two molecules of water ($CaSO_4 \cdot 2H_2O$). The removal of the two molecules of water produces the mineral anhydrite ($CaSO_4$). The mineral anhydrite (anhydrous calcium sulfate) can exist in two forms, one which hydrates with water and the other, an unreactive species which shows little or no tendency to hydrate in the presence of water. The mineral which hydrates in water is termed ‘soluble anhydrite’ and the other form ‘insoluble anhydrite’. In Fig. 3, a sample of calcium sulfate dihydrate was subjected to differential thermal analysis (DTA) to determine the parameters of its dehydration. The sample was heated at $20°C\,min^{-1}$. Hygroscopic water was removed between 60 and 100°C. Water of crystallization was removed

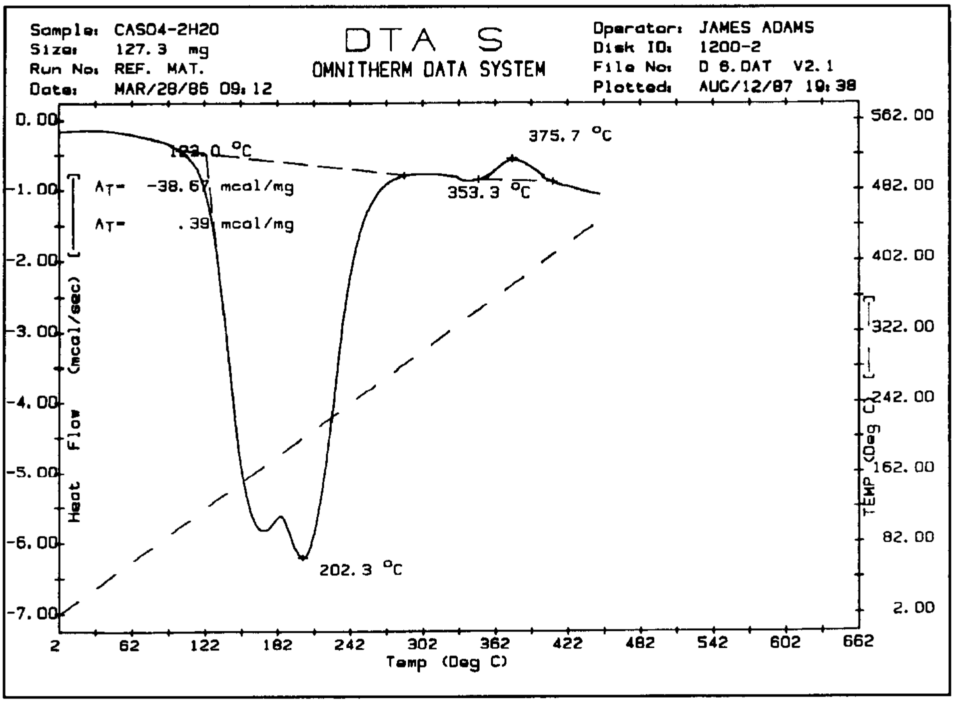


Fig. 3. DTA of calcium sulfate dihydrate.

to produce the hemihydrate form ($CaSO_4 \cdot 0.5H_2O$). The endothermic peak representing this phase has an extrapolated onset temperature of 123.0°C with the hemihydrate reaction ending at 163.0°C. The second peak of the doublet at 202.3°C represents the loss of $0.5H_2O$ to form soluble anhydrite ($CaSO_4$). The peak temperature of 203.3°C has an endothermic energy of 38.67 mcal mg^{-1}. The exothermic peak between 353.3 and 375.7°C represents the phase change to insoluble anhydrite. Continued heating above 1100°C reduces the insoluble anhydrite to CaO and sulfur trioxide gas (SO_3).

Hydration of gypsum

The setting and hardening of gypsum mortar simply requires the addition of water to the hemihydrate and/or the soluble anhydrite to form a paste. Lea explains the process of crystallization as follows:

> The deposition begins at some point and a series of changes repeats itself, the hemihydrate dissolving, becoming further hydrated, and then depositing crystals of dihydrate. This process requires a limited amount of H_2O thereby allowing the crystal nuclei to form a composite mass, facilitating the hardening process.

Hanson [5] concluded that the process is carried out in two stages. First, fine particles of anhydrite react with H_2O to form a colloidal layer.

Second, the layer breaks up to form nuclei, thus facilitating the crystallization into a tightly interlocking mass of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$).

STRENGTH OF GYPSUM AND LIME MORTARS

Gypsum mortar

Livingston et al. [6] have reviewed the literature pertaining to the use of gypsum in historic architecture. Especially interesting is their review of work by Sabnis and White. They found that the ultimate strength of gypsum mortar is based largely on the water-to-gypsum ratio and on the aggregate-to-gypsum ratio. Sabnis and White report that increasing the aggregate ratio from zero to 1.2 reduced compression strength by up to 50%. An increase in water ratio from 0.3 to 0.4 also reduced compressive strength by 27–34%.

Livingston et al. compare the strength properties of gypsum mortars with those of cementitious mortars. Sabnis and White report a compressive strength of 2000 psi for gypsum under experimental conditions and a tensile strength of about 200 psi (split cylinder test). They state that the main deterrent to the widespread use of gypsum in Europe with its wet climate is the high solubility factor (nearly 40 times that of lime).

Lime mortar

Unlike gypsum mortars which develop an interlocking crystal structure in the presence of water, lime mortars must react with CO_2 to form calcite crystals by the process of recarbonation. The complete process for lime is

$$CaCO_3 + \Delta_{\text{heat}} \rightleftharpoons CaO + CO_2 \uparrow$$

$$CaO + H_2O = Ca(OH)_2$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Morehead [8] states that the carbonation process results from an exchange of water vapor for carbon dioxide, and that the rate of exchange is slow as a result of low permeability. This low transfer rate might require years for complete carbonation to occur. The earlier literature reports that ancient lime mortars are uncarbonated in walls of other than medium thickness, whereas the present research found that nearly all medieval mortars examined had reached near total recarbonation, though the rate of recarbonation has not been investigated. In contrast, gypsum mortars harden quite rapidly. The expansion of gypsum paste is approximately 0.5%, in comparison to lime paste which shrinks approximately 0.35%. Due to shrinkage, lime mortar requires the addition of larger amounts of aggregate; however, the aggregate increases porosity, thus facilitating transfer of CO_2 gas. Morehead reports typical values for compressive strength in lime mortar at 1,340 psi with tensile strength at 50–100 psi. Lea [4] reports that lime and sand mortars (1:3 ratio) develop tensile strengths of only 22 psi in an atmosphere of 50% relative humidity, increasing to 48 psi with an increase to 100% relative humidity. The literature reports that the strength of gypsum mortar is superior to that of lime mortar, especially in tension.

Portland cement mortar: a definition

Early in the nineteenth century (1824), it was discovered that burning calcareous and argillaceous materials at a clinkering temperature (1350°C) and subsequently grinding the cooled clinker produced a highly reactive product valuable in cement and mortar making [11]. The reactive agents, tricalcium silicate (C_3S), β-dicalcium silicate (β-C_2S) and tricalcium aluminate (C_3A) result from the reaction between calcium oxide (CaO) and thermally altered clays. During the hydration phase of these products, chemical reactions occur which cause rapid hardening. The most important reactions include the calcium silicates. According to Lea [4], mature paste is composed of colloidal silicate hydrate (CSH) (70% by volume) and calcium hydroxide (20% by volume). During the initial reaction, C_3A hydrates rapidly and if gypsum is not added, rapid setting will occur. Calcium sulfate (gypsum) reacts with tricalcium aluminate to form calcium sulfoaluminate hydrate (ettringite). In this reaction, C_3A is rendered temporarily inactive. The use of calcium sulfate to retard setting is therefore relevant to the chemical characterization of medieval mortars that contain both thermally altered clay and gypsum.

METHODS OF ANALYSIS

Thermal analysis

The analysis of aged mortars is facilitated by the use of thermal analytical techniques, both differential thermal analysis (DTA) and thermogravimetry (TG). Thermal analysis involves measuring the thermal variations associated with the physical and chemical modifications which occur during the heating of the specimen. These thermal transformations include those associated with dehydration, oxidation and decomposition. In addition, crystalline transitions can be observed as these changes are accompanied by exothermic and endothermic peaks on the DTA curve. The results obtained by the DTA method were reinforced by the use of TG studies in which the mass of the sample is monitored as a function of temperature. Medieval mortars lend themselves to such analysis due to the decomposition of several phases. They include decomposition of portlandite ($Ca(OH)_2$), calcium carbonate ($CaCO_3$), calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) and clay minerals such as illite. Thermal analysis can also be used to identify those fractions of such low crystallinity that X-ray diffraction (XRD) fails to identify. Thermal analysis is shown to be a useful tool in determining the original bonding and compressive strength of medieval mortar.

Instrumentation

Differential thermal analysis (DTA)

A Stone differential thermal analyzer with an Omnitherm microprocessor was used in the DTA study. Nickel sample holders were used. The samples ranged from 120 to 200 mg and the heating rate was 20°C min^{-1}. The heating was done in a static atmosphere of air and the reference material was α-Al_2O_3.

Thermogravimetric analysis (TG)

A Stanton Redcroft Thermal Balance (TG-720) with an Omnitherm Microprocessor was used in the TG study. The sample holder was platinum. The mass of the sample was 2 ± 0.5 mg, and the heating rate was 20°C min^{-1}. The heating was done in a dynamic atmosphere of dry nitrogen with a flow rate of 150 ml min^{-1}.

X-ray diffraction

The pan fractions of the samples were examined by the X-ray diffraction method. X-ray powder diffraction establishes qualitatively the presence of minerals which exist in a crystalline state. The most common phases present in the mortars are calcium carbonate ($CaCO_3$), portlandite ($Ca(OH)_2$), silicon dioxide (SiO_2), calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) and clay minerals such as illite.

PREPARATION OF SAMPLES

Separation of mortar

Prior to performing destructive testing (DTA and TG), the mortar samples were physically separated to gather data on aggregate grading. The samples were prepared for sieving by carefully crushing the mortars. Subsequent sieving was done in a vibratory separator. After crushing, each sample was sieved using a series of ASTM sieves numbered 4, 8, 16, 30, 50, 100, and 200. The material passing the 200 sieve was collected in a pan. Each sample was vibrated for 20 min. The fractions were then weighed and recorded as weight retained and as percentage of total weight retained in each sieve fraction. These data were used to develop retained weight curves and average density plots.

Drying of mortar

Prior to thermal analysis, the mortar specimens were dried at 95°C for 24 hours to remove hygroscopic water. The samples were then stored in a desiccator to preserve their state of dehydration.

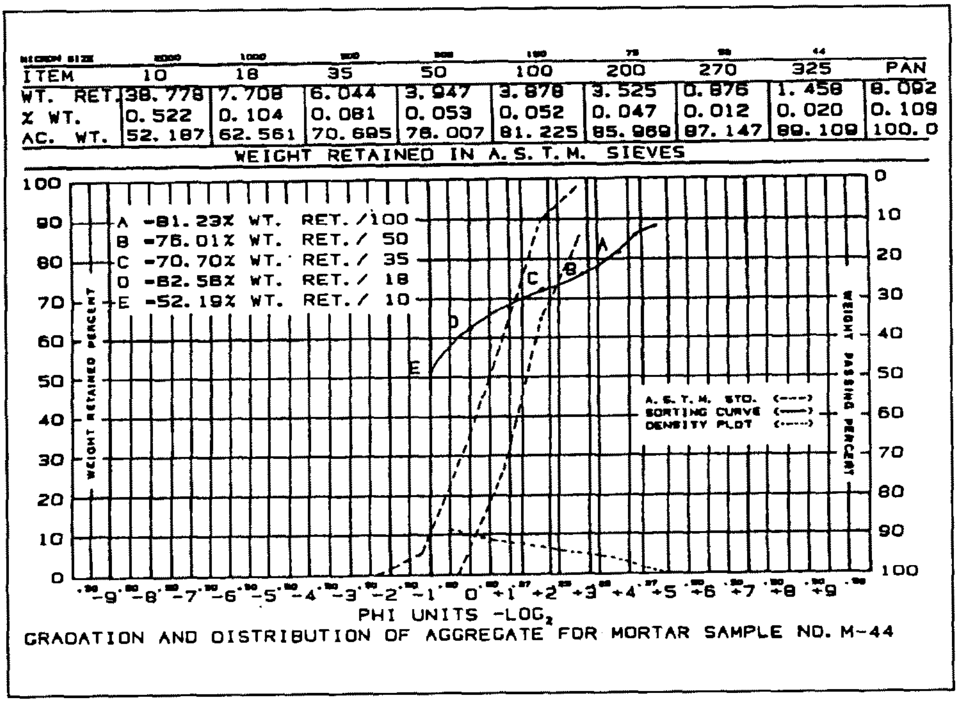
Standards

Laboratory grade specimens of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), portlandite ($Ca(OH)_2$) and calcium carbonate ($CaCo_3$) were used as standards for comparative studies of the mortars.

DISCUSSION OF DATA

The data on aggregate sorting was used to establish retained weight curves and average density plots.

The conclusions drawn from these data infer that medieval mortars in French Gothic cathedrals were frequently subjected to local distress and crushing due to poor aggregate sorting. The development of a crystalline matrix between the calcareous component and the inert sand fraction was not apparent to the medieval mason. The retained weight curves and the average density plot in Fig. 4 reveal the presence of poorly sorted



MICRON SIZE	2000	1000	[illegible]	[illegible]	[illegible]	75	[illegible]	44	
ITEM	10	18	35	50	100	200	270	325	PAN
WT. RET.	38.778	7.708	6.044	3.947	3.878	3.525	0.876	1.458	8.092
% WT.	0.522	0.104	0.081	0.053	0.052	0.047	0.012	0.020	0.109
AC. WT.	52.187	62.561	70.695	78.007	81.225	85.969	87.147	89.109	100.0

WEIGHT RETAINED IN A. S. T. M. SIEVES

GRADATION AND DISTRIBUTION OF AGGREGATE FOR MORTAR SAMPLE NO. M-44

Fig. 4. Retained weight curve and average density plot of mortar from Laon Cathedral.

aggregate in the admixture from the cathedral at Loan. Thermal analyses (DTA and TG) of this mortar show a carbon dioxide content of 39.19% or 89.07% calcium carbonate, using molecular proportions, and are shown in Figs. 5 and 6 respectively. This mortar, though containing 89.07% carbonate, has not developed good bonding with the aggregate. Average density plots for Chartres and Paris shown in Figs. 7 and 8 are typical of mortars from these cathedrals.

The clay mineral (illite) found in the mortars from Chartres cathedral, is seen in the X-ray diffraction pattern of Fig. 9. The clay is presumed to have been thermally altered during the lime burning process. The temperature to calcine limestone (less than 900°C) is above that required to remove molecular water from illite (dehydroxylation). Dehydroxylation is a reversible reaction and is unstable. However, at about 900°C, dehydroxylated illite becomes more stable. Meta-illite reacts with calcium hydroxide to impart hydraulic properties to lime mortar.

Livingston et al. [6] refer to the reaction between clay and lime and suggest that calcium silicate hydrate (CSH), a product of the reaction between calcium oxide (CaO) and clay brought to a clinkering temperature of 1350°C, must be present to induce hydraulic properties in mortar (setting in the presence of water). They comment on the presence of gypsum in mortars taken from the cathedrals of Chartres and Bourges.

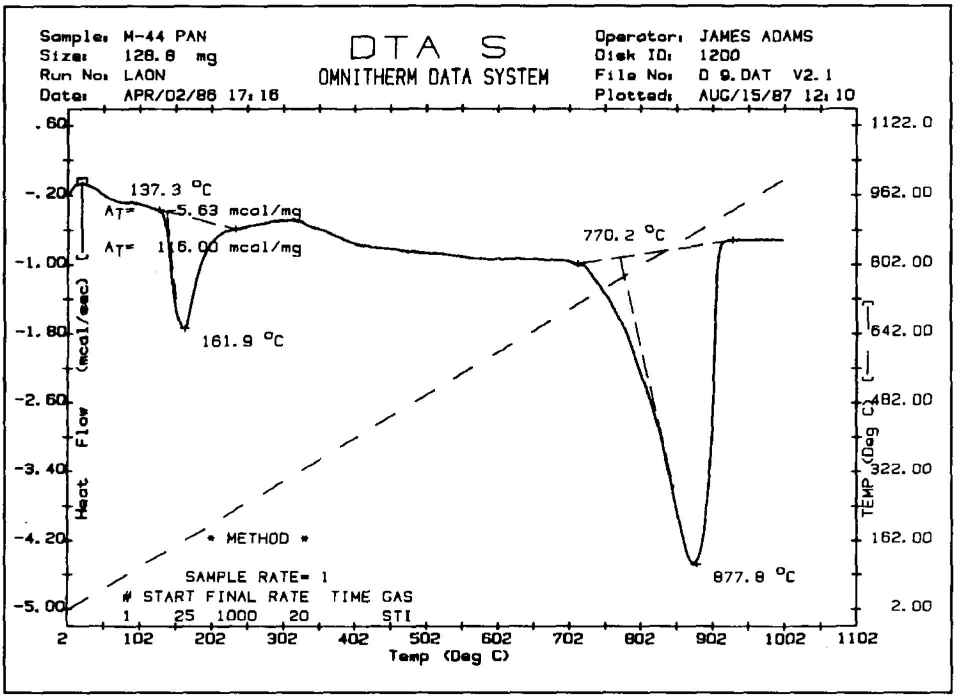


Fig. 5. DTA of mortar from Laon Cathedral.

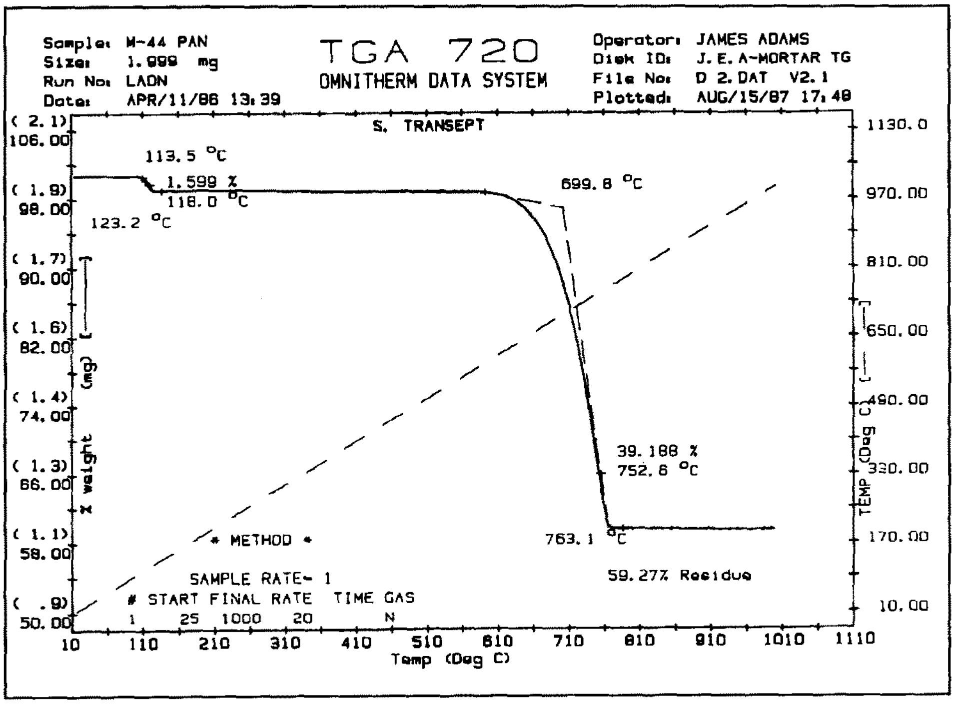
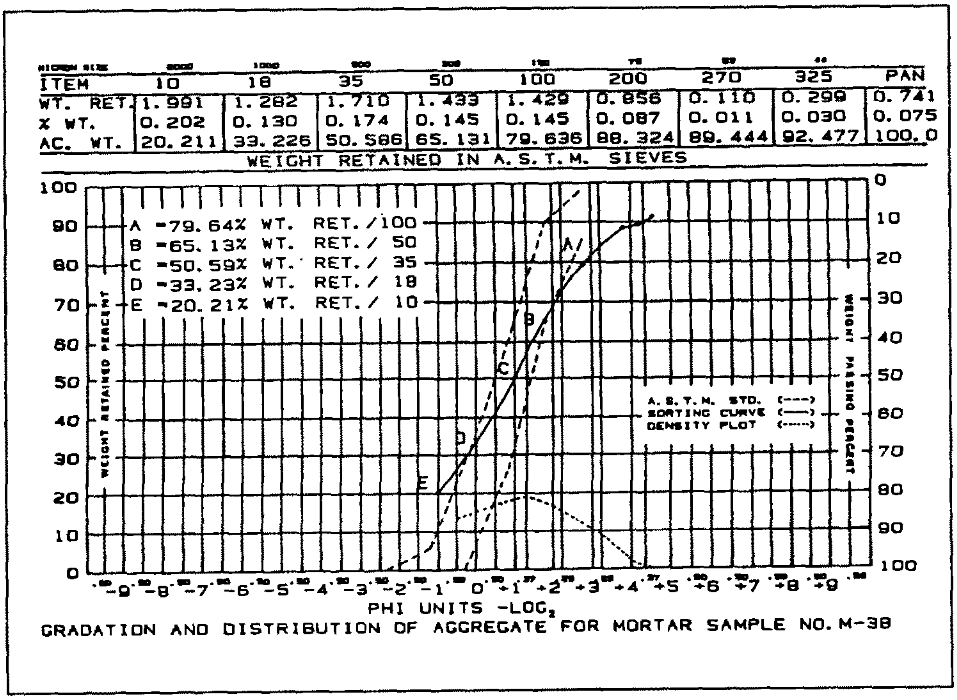


Fig. 6. TG of mortar from Laon Cathedral.

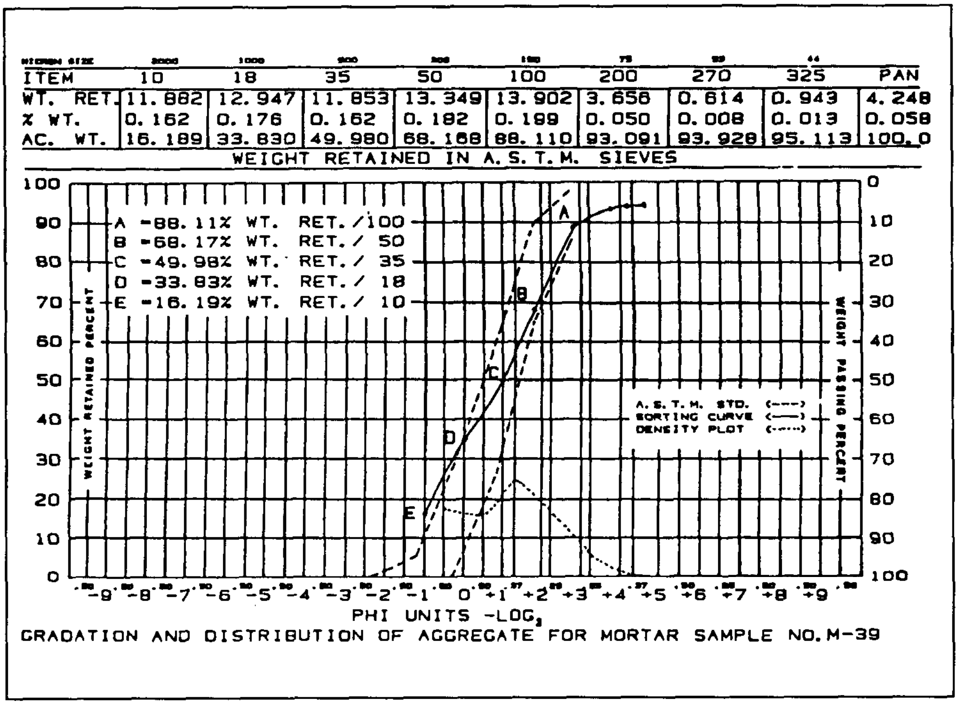


ITEM	10	18	35	50	100	200	270	325	PAN
WT. RET.	1.991	1.282	1.710	1.433	1.429	0.856	0.110	0.299	0.741
% WT.	0.202	0.130	0.174	0.145	0.145	0.087	0.011	0.030	0.075
AC. WT.	20.211	33.226	50.586	65.131	79.636	88.324	89.444	92.477	100.0

WEIGHT RETAINED IN A.S.T.M. SIEVES

A -79.64% WT. RET./100
B -65.13% WT. RET./ 50
C -50.59% WT. RET./ 35
D -33.23% WT. RET./ 18
E -20.21% WT. RET./ 10

Fig. 7. Average density plot of mortar from Chartres Cathedral.



MICRON SIZE	2000	1000	500	300	150	75	53	44	
ITEM	10	18	35	50	100	200	270	325	PAN
WT. RET.	11.882	12.947	11.853	13.349	13.902	3.656	0.614	0.943	4.248
% WT.	0.162	0.176	0.162	0.182	0.189	0.050	0.008	0.013	0.058
AC. WT.	16.189	33.830	49.980	68.168	88.110	93.091	93.928	95.113	100.0

WEIGHT RETAINED IN A.S.T.M. SIEVES

A -88.11% WT. RET./100
B -68.17% WT. RET./ 50
C -49.98% WT. RET./ 35
D -33.83% WT. RET./ 18
E -16.19% WT. RET./ 10

Fig. 8. Average density plot of mortar from Notre-Dame Cathedral.

Referring to Adams and Kneller's observation [9] that gypsum, present in these mortars, might have acted as a retardant, they state: Adams and Kneller's "... argument is based on the identification of illite as a component, leading to the possibility that aluminum and silica from the calcined clay would have produced a natural pozzolan. However, their thermal analysis fails to identify C–S–H compounds in the mortar." In

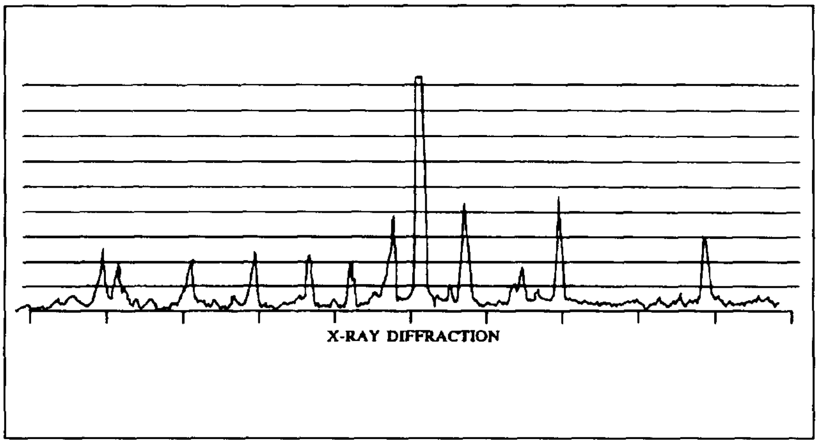


Fig. 9. X-ray diffraction pattern of mortar from Chartres Cathedral showing the presence of illite.

this regard they are correct: C–S–H compounds were not identified in the mortars from Chartres. A pozzolan is defined as a siliceous or alumino-siliceous material. Boynton [10] states that these materials in themselves (fired clay tile or clay brick) possess "... little or no cementitious value, but that in finely divided form and in the presence of moisture will chemically react with alkali or alkaline earth hydroxides..." These reactions take place at ordinary temperatures to form compounds possessing cementitious properties.

The Centre de Recherches sur les Monuments Historiques in Paris provided mortar samples from the ancient Basilique de Saint-Denis. The thermogram in Fig. 10 shows a weight loss and a peak temperature of 753.2°C. This weight loss can be characterized by

$$\frac{56}{\mathrm{CaO}}+\frac{44}{\mathrm{CO_2}}=\frac{100}{\mathrm{CaCO_3}}$$

$$44\times\frac{100}{100}=44\%\ \mathrm{CO_2}$$

$$\frac{30.128\%}{44\%}=68.47\%\ \mathrm{CaCO_3}$$

$$68.47\%\times 56=38.34\%\ \mathrm{CaO}$$

$$\mathrm{Residue}=65.22\%-[38.34\%\ \mathrm{CaO}]=26.88\%$$

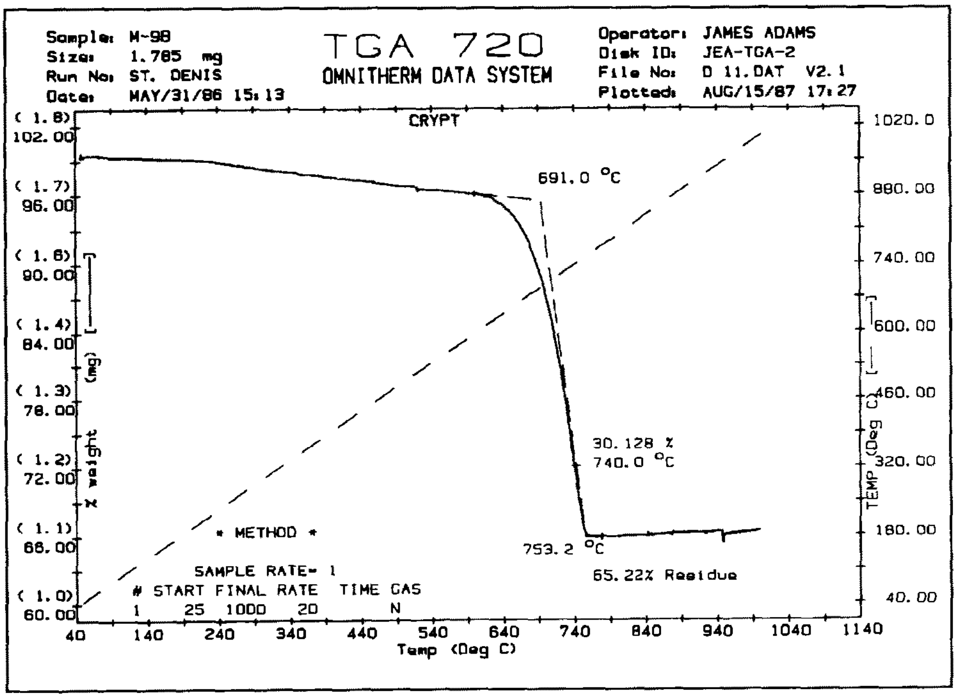


Fig. 10. TG of mortar from the Basilique de Saint-Denis.

The remaining residue (26.88%) is composed of other materials including silicon dioxide (SiO_2).

The Saint-Denis mortar dates from the eighth century. However, recarbonation has not progressed to the same extent as in the mortars of the thirteenth century, although the mortar is extremely well consolidated and possesses a higher compression strength than any of the other mortars in this study. Two reasons might account for this paradox. Firstly, the Saint-Denis mortar contains finely sorted aggregate (non-retained in an ASTM 10 sieve). Secondly, there is compelling, though not definitive, evidence that suggests the use of pozzolanic mortars at Saint-Denis. This mortar contains a siliceous material which is believed to be a man-made fired clay brick or tile.

The pozzolanic activity of a crushed tile and its ability to increase the hydraulicity of a lime-mortar mixture was demonstrated by Davey [11]. He crushed tile and mixed it with a non-hydraulic high-calcium lime (98% CaO) in a lime-to-crushed-tile ratio of 1:3. Small beams measuring 1 inch by 1 inch were made from the admixture. These beams were stored at 20°C for 28 days, 56 days and 90 days, respectively. After soaking in water for 30 min, the beams were broken by transverse bending (at each of the three ages). The tensile strength of the mortars was determined: after 28 days, 54 psi; after 56 days, 196 psi; after 90 days, 279 psi.

The siliceous component of the Saint-Denis mortar conforms to the definition for finely divided material (passing an ASTM 200 sieve).

CONCLUSIONS

Comparison of eighth-century mortar from Saint-Denis with lime-based mortars of the twelfth and thirteenth centuries confirms that the extent of recarbonation alone will not establish the comparative strength of aged mortars. In addition to determining the carbon dioxide (CO_2) content, these mortars must be analyzed for the presence of thermally altered clays and the presence of other minerals, in particular, calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) which can occur as a result of weathering (sulfur dioxide in rain water reacting with calcium carbonate), or as an addition through the conscious effort of the medieval mason.

X-ray diffraction and thermal analysis show positive evidence of gypsum in mortars from Chartres and Bourges. The evidence supports the conclusion that gypsum was added to these mortars. It is suggested that the possible reasons for the use of gypsum were, first, to replace lime mortars with faster setting gypsum mortars, and second, because the calcination of gypsum requires less fuel and has a higher yield than limestone.

ACKNOWLEDGMENT

Grateful acknowledgement is given to the Ministère de Culture, France, for valuable assistance in the collection of the mortar samples.

REFERENCES

1 P. Abraham, Les donneès plastiques et functionelles du probleme de l'ogive, Recherches No. 1: Le Probleme de l'ogive, Paris: Centre International des Institutes de Recherches, 1939.
2 W. Wallace, Ancient Egyptian Materials and Industries, London, 1865. Quoted in F.M. Lea, The Chemistry of Cement and Concrete, Edward Arnold Ltd., London, 1956, p. 2.
3 A. Choisy, L'Art de Batir chez les Egyptians, Paris, 1904.
4 F.M. Lea, The Chemistry of Cement and Concrete, Edward Arnold Ltd., London, 1956, pp. 216–217.
5 W.C. Hanson, The setting and hardening of gypsum plasters, Mater. Res. Stand., 3 (1963) 359–363.
6 R. Livingston, A. Wolde-Tinsae and A. Chaturbahai, The use of gypsum mortars in historic buildings; structural repair and maintenance of historic buildings II. Proceedings of the Second International Conference, Seville, 1991, Vol. 1, pp. 157–165.
7 C.M. Sabnis and R.N. White, A gypsum mortar for small scale models, J. Am. Concr. Inst., (1974) 767–774.
8 D.H. Morehead, Cementation by the carbonation of hydrated lime, Cem. Concr. Res., 16 (1986) 700–708.
9 J.E. Adams and W.A. Kneller, in P.G. Marinos and G.C. Koukis (Eds.), Thermal Analysis (TA) of Medieval Mortars from Gothic Cathedrals of France. The Engineering Geology of Ancient Works, Monuments and Historic Sites, A.A. Balkema, Rotterdam, Vol. 2, 1988, pp. 1019–1026.
10 R. Boynton, Chemical Technology of Lime and Limestone, Wiley, New York, 1980, p. 549.
11 N. Davey, Building materials in antiquity, Chem. Ind. (1950) 43.