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THERMAL ANALYTICAL INVESTIGATION OF ANCIENT MORTARS FROM GOTHIC CHURCHES

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The use of thermal analysis in studying ancient mortars in English cathedrals is explained. Thermal analysis can be used to investigate both mortar and stone in dated structures. Analysis of ancient mortars show that though recarbonated, they remain soft, yielding to structural deformations. The use of hard (cement mortar) in modern renovation can result in micro-cracking in the stone and subsequent chemical attack from the atmosphere. Contrary to the literature, data developed in the present study suggests that most medieval mortars have reached a near total state of recarbonation.

Keywords: ancient mortars, structural deformations

Introduction

The presence of gypsum in historic masonry is widely attributed to atmospheric pollution accompanied by chemical reaction between lime mortar and sulphur dioxide. The present study supports the conclusion that medieval masons made wide use of gypsum in transitional architecture (Romanesque to Gothic).

Mortar is a composite material, consisting of a continuous matrix of cement paste and aggregate. Behaviour under load is affected by its physico-chemical properties and the manner in which these properties evolve with time. Migration of contaminants into the matrix is partly dependent on the development of micro-cracking in the matrix. The matrix structurally deforms under load (observed as micro-cracking). Such deformations can be accompanied by failure of the mortar paste-aggregate bond. Excessively large aggregate particles in dated masonry can also lead to local distress such as cracking due to point pressure. Irreversible deformation of this type can result in non-predictable stress in composite struc-

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tures. Load analysis of stone and mortar is particularly dependent on their behaviour in this inelastic range of deformation. Mechanical loading and chemical reactions both initial and time-dependent can lead to inelastic deformations. Such loading normally resolves itself in a state of equilibrium ; however, failure by fracture and or crushing and sliding can occur.

Mortar chemistry

Lime

The hydration of lime is a consequence of the chemical reaction between CaO and H_2O to produce $Ca(OH)_2$. The reactivity of CaO is highly dependent on the way in which limestone is burnt or decarbonated. Excessive burning temperatures produce oxides of high shrinkage, low porosity and low chemical reactivity, whereas lower burning temperatures produce oxides of low shrinkage, high porosity and high chemical reactivity. These limes are referred to as 'hard burned' or 'soft burned' respectively.

Hard burned or impure lime might require years at atmospheric pressure and temperature for complete hydration to occur. In addition, other factors can retard hydration: (i) chemical impurities coat the surface of lime particles with a slag making the oxide impervious to the absorption of water; (ii) increasing the quantity of water will reduce the heat of reaction and retard the rate of hydration in the diluted mixture.

Gypsum

Calcium sulphate occurs in three forms: gypsum ($CaSO_4 \cdot 2H_2O$), bassanite ($CaSO_4 \cdot 1/2H_2O$) and anhydrite ($CaSO_4$). Anhydrous calcium sulphate can exit in two forms, soluble anhydrite and anhydrite. Bassanite and soluble anhydrite are similar in structure, both consisting of Ca^{2+} and SO_4^{2-} in an open framework. Both structures have continuous channels in one direction but, in the hemihydrate, the channels contain water. When gypsum is dehydrated [1] water is removed zeolitically and the Ca–SO_4 framework shrinks until 1/2 molecule of water remains. Figure 1 illustrates removal of hygroscopic water between 60° and 100°C, followed by the water of crystallization during the transition to the hemihydrate form. The endothermic peak representing this phase has an extrapolated onset temperature of 123.0°C. The second peak of the doublet at 202.3°C, represents loss of the remaining $1/2H_2O$ to form 'dehydrated hemihydrate' ($CaSO_4$).

The exothermic peak between 353.3° and 375.7°C, represents the phase change from soluble to insoluble anhydrite (β–$CaSO_4$).

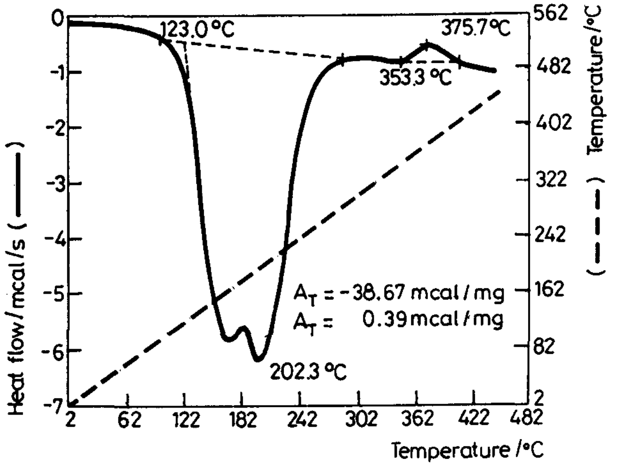

Fig. 1 DTA curve of gypsum. Sample mass 127 mg, heating rate 10 deg·min^{-1}, static air, Ni sample holder

Medieval mortars

Mortar formulas were based on data obtained from thirty-four specimens of medieval mortar from cathedrals in England and France and five specimens of modern mortars currently in use at Salisbury Cathedral. Material passing a 100 mesh sieve was recorded as a percentage of the total sample. Proportions of hydrated lime and gypsum in these mortars were determined by DTA and TG.

Replicated mortars

Materials

The mortars were made with commercially available hydrated high-calcium lime (type N) meeting ASTM specification C 207-79 (CaO 95%) and commercially available gypsum meeting ASTM specification C 28. All mortar specimens were produced using the same batch of lime and gypsum. The lime and gypsum were stored in sealed containers between experiments. Commercially available clay was heated in an electric muffle furnace to 900°C to produce metamontmorillonite which was used as an additive in certain preparations. Commercially available sand and aggregate were sieved and graded to match ASTM specification C 144-81. All preparations were made with deionized water.

Sample preparation

For each mortar, four sets of three samples each were prepared in accordance with ASTM specification C 305-82. Each mortar mixture contained 2800 g dry ingredients and 500 ml of deionized water. The dry materials were stored between 20° and 27.5°C and were kept within this temperatures range during preparation and also at a relative humidity of not less than 50%.

Testing

Compression testing of the mortar specimens was carried out at 7, 14 and 28 days using a Tinius-Olsen compression tester and in compliance with ASTM specification C 109-87. The pacer rate was set at 30% and the unit was set in the low-range. The testing unit was set to record the compression strength of samples having a surface area of 4 square inches. The loading rate was applied without interruption until failure occurred. Three cubes of each mortar sample were tested and the average of the three strengths were recorded (Table 1). The loading was applied so as not reach failure in less than 20 seconds, nor more than 80 seconds. Strengths which varied more than 10 percent were not used in the averaging. Table 2 shows the compression strength of 28 days mortar specimens that were exposed to an atmosphere of CO_2 for 24 hours. There was a significant increase in compression strength in these mortars.

Discussion

Much of the literature on architectural conservation relies heavily on assumptions regarding the physico-chemical properties of ancient mortars. It is generally accepted that medieval mortars are composed simply of slaked lime and sand with little or no inherent strength. Therefore, mortar as a constituent part of the structural system has been disregarded in nearly all structural analysis of Gothic cathedrals [2, 4]. The present study suggests that modern cement mortars are not compatible with dated masonry as a restoration material partly due to its hardness and partly due to its reaction with calcium sulphate to form ettringite [5]. The

Table 1 Compression test results

Sample No.	Lime / %	Gypsum/ %	L/G ratio /%	7 days psi	14 days psi	28 days psi	Incr / %	28 days CO_2 /psi
101	7.38	2.37	75.7/24.3	65	67	70	7.69	108
102	5.86	1.18	83.2/16.8	55	60	59	3.63	100
103	12.30	0.0	100/0	65	70	74	13.84	136
104	18.33	1.42	92.8/7.2	93	140	167	79.56	445
105	**5.59**	**0.06**	**98.9/1.1**	**51**	**55**	**54**	**5.88**	**NA**
106	**3.22**	**0.64**	**83.4/16.6**	**48**	**53**	**50**	**4.16**	**NA**
107	10.84	0.98	91.7/8.3	90	98	116	28.88	180
108	7.34	0.14	98.1/1.9	78	87	94	20.51	122
109	8.09	1.78	82.0/18.0	70	94	100	42.85	112
110	10.35	0.91	92.0/8.0	71	85	99	25.35	118
111	14.32	0.23	98.4/1.6	50	81	118	136.0	185
112	2.98	0.0	100/0	30	37	36	20.0	60
113	4.21	0.24	92.5/7.5	47	51	53	12.76	86
114	4.08	0.26	94.0/6.0	33	57	59	69.69	84
115	No DATA collected							
116	5.08	1.02	83.3/16.7	34	60	63	85.29	90
117	9.79	0.78	92.6/7.9	66	75	83	25.75	224
118	3.89	0.54	87.8/12.2	60	68	70	16.66	140
119	5.09	0.49	91.2/8.8	36	65	63	91.66	73
120	**No DATA collected**							
121	13.04	0.09	99.3/0.7	80	110	123	53.75	163
122	2.44	0.03	98.8/1.2	48	56	57	18.75	61
123	5.94	0.34	94.6/5.4	42	59	74	66.66	147
124	21.34	0.75	96.6/3.4	67	85	120	79.10	545

psi = pounds per square inch

Table 2 CO_2 test results in psi

Sample	7 days	14 days	28 days	28 days / CO_2	Lime /%
104	93	140	167	445	18.33
117	66	75	83	224	9.79
124	67	85	120	545	21.34

results of the present study thus can be used to develop recommendations for the formulation of restoration mortars.

Test mortars

Under load the cement-aggregate matrix is subjected to irrecoverable deformation. Structurally, the deformation is accompained by failure at the mortar paste-aggregate interface. Deformation of this type can lead to non-predictable failures. Load analysis of mortar is dependent on behaviour in the inelastic irreversible range of deformation. Under load, mortar is initially linear in its behaviour; then due to failure of the mortar paste-aggregate interface, inelastic non-linear deformations occur. Heyman [4] has said: 'If, on striking the centering for a flying buttress, that buttress stands for 5 minutes, then it will stand for 500 years'. The fact that the buttress stands for 5 minutes might only suggest that a statistically admissible thrust line can be found within the masonry during the initial period. Fitchen [6], the noted authority on medieval construction practices writes that medieval masons carefully lowered the centering beneath the vault ribbing (the centering was not removed at this time) shortly after completion of the vault webbing. This procedure applied initial loading to the rib mortar joints allowing deformation within the elastic range.

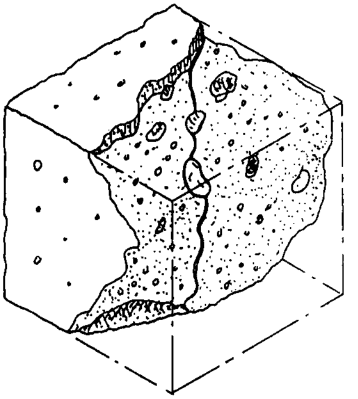

Fig. 2 Replicated mortar, Salisbury Cathedral

Data from the present study demonstrates the response to loading by mortar test specimens. Test specimen 137 is shown in Fig. 2. The drawing represents test mortar 137 after compression testing. The compression strength was recorded at 63 psi. The fracture which extends through the centre of the mortar is due to the linear response of vertical loading. The outer shell (1/16 to 1/8 inch) is composed of aggregate cemented with calcium carbonate. The shell formed during 28 days of exposure to the atmosphere. Figure 3 shows specimen 137 rotated 90° clockwise. The vertical fracture along the corner is the extension of the fracture shown in Fig. 2. All of the test mortars failed in a similar mode, and under a microscope fractures are present which are not apparent to the unaided eye. At the structural level, micro-cracking is evident and the paste aggregate matrix shows extreme distress. The large particles are loose and the carbonated shell is detached at the interface of the noncarbonated and the carbonated material. The test mortar is representative of a mortar obtained from the tower (200') at Salisbury Cathedral.

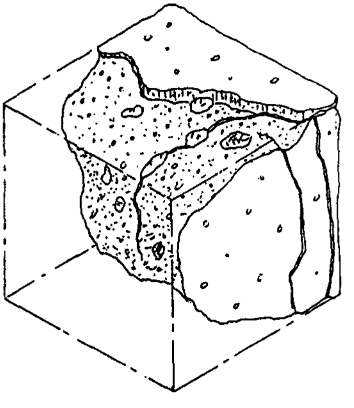

Fig. 3 Replicated mortar, Salisbury Cathedral

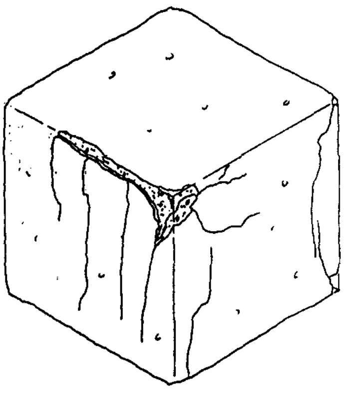

Fig. 4 Replicated mortar, Salisbury Cathedral

Figure 4 represents test mortar 104 obtained from the parapet (80') at Salisbury Cathedral. Test mortars 137 and 104 contained 17.74 and 18.33 percent calcium hydroxide respectively. In contrast to the 63 psi compression strength obtained with test mortar 137, test mortar 104 (after accelerated carbonation) reached a compression strength of 445 psi at 28 days. The specimen fractured under load; however, the internal paste aggregate matrix maintained a higher level of integrity. Both test mortars contain less than 1% gypsum. The disruption of the carbonated shell on 104 is less severe than 137 and the internal matrix is quite hard. Test mortar 104 contains no aggregate more than 1.19 mm. In contrast 2.76% of the aggregate in 137 was retained in the No. 8 sieve (2.38 mm).

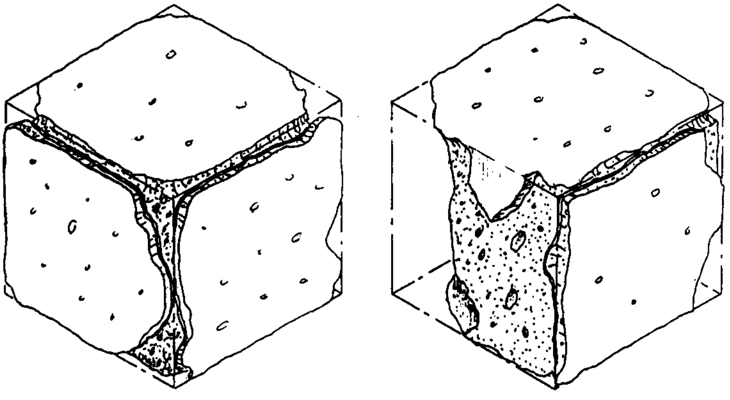

Fig. 5 Replicated mortar, Salisbury Cathedral

Figure 5 is a drawing showing two views of test mortar 125 after compression testing. This specimen reached a compression strength of 90 psi at 28 days. The mode of failure was the same as 137 and 104; first, linear fracture and then structural failure of the paste aggregate matrix. Test mortar 125 contains 17.22% calcium hydroxide and 5.76% of its aggregate was retained in the No. 8 sieve (2.38 mm).

Conclusions

Contrary to the literature, it is concluded from the present study that medieval lime mortars have reached a near total state of carbonation. Further, in mortars exposed to the atmosphere, significant increase in strength was observed during the 28 days testing period. Though the data are limited by the size of the test, they support the conclusion that 95% of the aggregate in lime mortars should be smaller than 2.38 mm.

In addition to observed linear fracturing, mortars which have undergone compression in excess of their crushing strength undergo structural failure of bonding in the paste-aggregate matrix resulting in irreversible deformation. In the absence of cohesive bonding in the matrix and in the presence of linear fractures, permeability is increased. This condition might manifest itself in accelerated carbonation due to the increased rate of gas and liquid transfer in the matrix. Nevertheless, carbonation of lime in such a structure will not increase its strength. The phenomenon of irreversible deformation can lead to non-predictable failures. Basically, loading can either resolve itself in a state of equilibrium or by structural failure of the mortar (fracturing or crushing). Such a failure can be accompanied by sliding and catastrophic failure of the masonry. It is clear that the action of the masonry is particularly dependent on the behaviour of mortar in the inelastic range of deformation.

Test mortars which were kept closed in plastic bags (not sealed) exhibited a high degree of ductility at 28 days. The surface of the two inch cube yielded to local pressure without accompanying fractures. It is concluded that lime mortar, confined within a masonry wall, will maintain a high degree of ductility for a protracted length of time thus allowing adjustment for static loads.

The use of gypsum beyond that required to establish early setting and reduced flow characteristics (occurring regardless of local conditions) will significantly reduce the state of ductility in non-carbonated lime mortar. It is concluded that in lime mortars, aggregate which possess a high degree of surface area for any paste-aggregate ratio will attain a higher compression strength than those with a lower surface area.

It is concluded that a minimum of 30 percent hydrated lime should be used in restoration mortars.

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Zusammenfassung — Es wird die Anwendung von Thermoanalyse bei der Untersuchung von alten Mörteln in englischen Kathedralen beschrieben. Sie kann zur Untersuchung sowohl des Mörtels als auch des Steines dieser alten Strukturen eingesetzt werden. Die Analyse der alten

Mörtel ergab, daß sie, obwohl sie rekarboniert sind, plastisch bleiben, was zu Strukturdeformationen führt. Der Einsatz von Hart(Zement)mörtel bei der jetzigen Renovierung kann eine Mikrorißbildung im Stein und einen nachfolgenden chemischen Angriff durch die Atmosphäre zur Folge haben. Im Gegensatz zu Literaturangaben wurde in dieser Untersuchung gezeigt, daß die meisten dieser mittelalterlichen Mörtel eine fast vollständige Rekarbonierung erreicht haben.