

THE USE OF TG TO MEASURE DIFFERENT CONCENTRATIONS OF LIME IN NON-HYDRAULIC LIME MORTARS

R. M. H. Lawrence¹, T. J. Mays², P. Walker^{1*} and D. D'Ayala¹

¹Department of Architecture and Civil Engineering, University of Bath, Bath BA2 7AY, United Kingdom

²Department of Chemical Engineering, University of Bath, Bath BA2 7AY, United Kingdom

A high speed method of thermal analysis was developed to allow the carbonation profile of lime mortars to be followed within a convenient time-frame. The loss in mass on heating, up to 700°C, of lime/sand mixtures of different proportions was related to the known quantity of lime in each mixture. It was shown that a heating rate of 50°C min⁻¹ produced data which had a very high correlation with known quantities of Ca(OH)₂. This method can be used to measure the extent of carbonation at varying depths through a lime mortar. This can be repeated at intervals to give an insight into the shape and extent of the carbonation front as it develops over time.

Keywords: carbonation front, lime mortar, thermal analysis

Introduction

Lime has been used as a binder in mortar for millennia; examples of its use have been found in Palestine and Turkey dating from 12000 BC [1]. Since the vast majority of historic buildings have been constructed using lime mortars, conservationists need to have a good understanding of how lime mortars perform in order to preserve the integrity of the structure. Lime mortars are most commonly made by adding water to a 1:3 lime:aggregate (B:Ag) ratio by dry material volume, but this ratio varies according to the desired properties of the mortar. Lime is manufactured by the calcination of limestone at a temperature of around 900°C. Lime can be either hydraulic (able to set under water) or non-hydraulic. Non-hydraulic limes set entirely through the process of carbonation, which is the reaction of calcium lime (Ca(OH)₂) or dolomitic lime (Ca(OH)₂·Mg(OH)₂) with atmospheric carbon dioxide (CO₂) to form carbonates (CaCO₃ or CaCO₃·MgCO₃). This process progresses from the exterior towards the core of the mortar, and can take many months or years to complete. Thermogravimetry (TG) is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature programme [2]. Although limited in scope to those reactions taking place with a change in mass, TG gives results that are intrinsically quantitative. Thus the measured mass losses will fully reflect the overall reaction taking place [3]. The first derivative of the TG curve (DTG) is effective in highlighting the onset and termination of individual reactions. Researchers into lime mortars gen-

erally use thermogravimetric analysis to measure the progress of carbonation by mixing a sample from the exterior with a sample from the core to produce an 'average' carbonation, Fig. 4. To do this ignores the fact that the exterior of a specimen, once carbonated, changes very little with time, whereas the core only carbonates at the very end of the process. A far better method would be to measure carbonation at intervals through the depth of the specimen. Researchers have not used this approach since it is considered to be a very time-consuming, and therefore expensive, process. This paper demonstrates the practicality of conducting a sequence of tests through the depth of a specimen within a convenient time-frame.

Conservation background

The setting of a hydraulic lime is a two-phase process. Initially there is a 'hydraulic set' resulting mainly from the formation of calcium silicate hydrates (C–S–H) and calcium aluminate hydrates (C–A–H). These reactions take place over a period of between 2 days (eminently hydraulic) and 20 days (feebly hydraulic) depending on the hydraulicity of the lime. Setting continues after this time through the carbonation of free hydroxide.

Non-hydraulic lime sets entirely through carbonation. This results in a much more extended setting time, lower compressive strengths and higher porosity, deformability, and water transport characteristics. These last four characteristics have proved to be useful in the field of conservation architecture. During the C19th and the first half of the C20th lime mortars were

* Author for correspondence: p.walker@bath.ac.uk

replaced by cement based mortars which were seen as stronger, more consistent, quicker setting and therefore 'better'. Whereas modern construction could be considered to have benefited from cement mortars in terms of speed of construction and reliability, their use on historic structures proved to be catastrophic [5]. Cement mortars are often more resistant to agents of decay than the historic substrate causing historic material to fail preferentially under stress. Cement mortars have low porosity which results in a build up of water and soluble salts at the substrate-mortar interface. This build up encourages salt crystallisation and freeze-thaw damage which can produce rapid deterioration in the substrate. Lime mortars, especially non-hydraulic lime mortars, do not produce these effects, and indeed can be used as a sacrificial material eliminating unwanted water and salt accretions. Failed mortar can then be replaced at intervals with no damage to the surrounding historic material. In addition, due to the slow carbonation process, lime mortars retain plasticity for extended periods of time. This means that structures built with non-hydraulic lime mortar accommodate movement and better retain their integrity when subjected to stresses.

Since non-hydraulic limes set entirely through carbonation, designers of such mortars need a good understanding of the carbonation process, and the ability to monitor the progress of carbonation over time.

Carbonation

Non-hydraulic high calcium lime is manufactured by burning a limestone which mainly consists of calcium carbonate (CaCO_3) at a temperature of about 900°C to produce calcium oxide (CaO), known as quick-lime. The quick-lime is then hydrated in water to form calcium hydroxide (Ca(OH)_2) known as lime.

On exposure to air the lime reacts with CO_2 to form CaCO_3 . This process is known as 'carbonation' and is responsible for the hardening of the mortar. Carbonation changes the microstructure of the mortar, not only improving the mechanical properties but also affecting the pore structure, and hence water transport characteristics. Ca(OH)_2 is alkaline, whereas CaCO_3 is neutral. The overall carbonation process can be described by the following reaction [6]:



The carbonate (molar mass of 74 g mol^{-1}) weighs about 35% more than the hydroxide from which it was formed (molar mass of 100 g mol^{-1}). There is also an increase in the volume of solids. Ca(OH)_2 (portlandite), which has a mass density of 2.24 g cm^{-3} and a molar volume of $33.0 \text{ cm}^3 \text{ mol}^{-1}$, is converted into CaCO_3 (calcite – or the more unusual crystalline forms vaterite and

aragonite), which has a mass density of 2.71 g cm^{-3} and a molar volume of $36.9 \text{ cm}^3 \text{ mol}^{-1}$, resulting in an increase in solids volume of about 12%. This increase in volume is accommodated in the pores of the mortar, which tends to reduce access to CO_2 . The heat generated by the reaction (the standard enthalpy of reaction at 25°C is -74 kJ mol^{-1}) may make a marginal contribution to the evaporation of water from the pores, which can have the effect of reducing the rate of carbonation, since water is the primary vehicle for this.

Within a mortar specimen, there is a transitional zone of mortar at varying carbonation levels between the fully carbonated mortar on the exposed surface and uncarbonated mortar deeper inside. Since the carbonation process affects the pore structure of the mortar, porosity and pore size distribution will also vary along the transitional zone. Carbonated mortar has higher compressive strength than uncarbonated mortar, hence there is also an equivalent variation in compressive strength across the profile. It is possible to follow this change in compressive strength by means of a drilling resistance measurement system (DRMS). This measures the resistance of the material to penetration by a drill operating at a fixed rotational speed and penetration rate. This resistance has been shown to be proportional to the compressive strength of the material [7]. The progression of this drilling resistance profile in a non-hydraulic lime putty mortar (B:Ag 1:3) between the ages of 14 and 28 days is illustrated in Fig. 1. (Data from work in progress at the University of Bath.)

There is no standardised technique for the measurement of carbonation of lime mortars [8]. Optical and scanning electron microscopy, wide-angle X-ray diffraction and Raman spectroscopy will detect the presence of portlandite, calcite, vaterite and aragonite but are unable to quantify them except in relative terms. Phenolphthalein staining will reveal the boundary between relatively carbonated material ($\text{pH} < 8.5$) and rela-

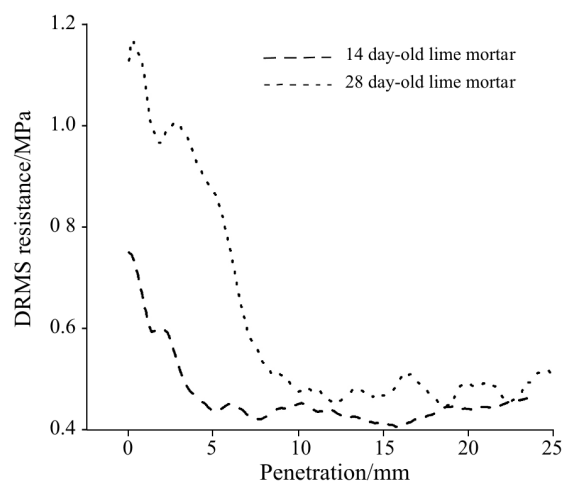


Fig. 1 Drilling resistance measurement system (DRMS) profile for a lime putty mortar at 14 and 28 days

tively uncarbonated material ($\text{pH} > 8.5$). Phenolphthalein ceases to reliably detect the presence of $\text{Ca}(\text{OH})_2$ at concentrations below $\sim 7.5\%$ by volume. Gravimetry can be used to measure the mass gain associated with carbonation, but this is only practical for unrealistically high CO_2 concentrations (3000 times normal atmospheric levels). Elemental analysis can quantify the percentage of hydrogen and carbon in a sample, but this is complicated by the difficulty in differentiating between adsorbed water and portlandite for hydrogen, and carbonated portlandite and other carbon bearing materials (such as aggregates) for carbon.

Thermogravimetry is a technique which gives the researcher into lime mortars very precise data on the quantities of $\text{Ca}(\text{OH})_2$ and CaCO_3 present in a sample. The thermal breakdown of a non-hydraulic lime is a very simple and well differentiated two-part process. $\text{Ca}(\text{OH})_2$ loses its chemically bound water between 350 and 550°C (dehydroxylation) (Table 1) and CaCO_3 loses its chemically bound CO_2 between 600 and 900°C (decarboxylation) (figures for 35% portlandite/sand vol/vol heated at 50°C min^{-1}). The spread of the temperature range is reduced as the percentage of portlandite reduces, and as the heating rate reduces.

Table 1 Dehydroxylation start and end temperatures for TG of lime/sand at 50°C min^{-1}

$\text{Ca}(\text{OH})_2$ / mass/mass/%	Dehydroxylation start $T/^\circ\text{C}$	Dehydroxylation finish $T/^\circ\text{C}$
30.45	353	567
24.32	351	562
19.04	360	565
13.86	350	542
10.12	350	523
5.03	359	506
2.44	353	505

TG/DTG analysis is therefore ideally suited since there are no overlapping reactions which require deconvoluting. The thermal breakdown of hydraulic lime mortars is more complex since the hydraulic elements break down at lower temperatures and overlap [9, 10] (Table 2).

The accuracy of thermal analysis for the quantitative determination of $\text{Ca}(\text{OH})_2$ and the conformity with chemical titration for the quantitative speciation of calcium in lime have been demonstrated [11, 12]. There is, however, no standardised procedure for measuring carbonation using TG. Methods currently in use vary from the most simple TG/DTG in static air at 20°C min^{-1} [13] to highly sophisticated TG/DTA/EGA in two different atmospheres at 10°C min^{-1} [14]. Tests are generally carried out on an 'average' sample, combining material from the edge of a specimen with mate-

Table 2 Thermal decomposition temperatures for TG of hydrated compounds at 20°C min^{-1}

Compound	Formula (S= SO_3 ; S=Si; A=Al; C=Ca)	$T/^\circ\text{C}$
calcium silicate hydrates	CSH types 1 and 2	95–120
ettringite	$\text{C}_4\text{ASH}_{12}$	125–135
monosulphate	$\text{C}_6\text{ASH}_{32}$	185–195
syngenite	$\text{K}_2\text{CaS}_2\text{H}$	265–275
gypsum (dihydrate)	CSH_2	160–186 (2 peaks)
calcium sulphate hemihydrate	$\text{CSH}_{1/2}$	185
calcium aluminates	CAH_{10} C_2AH_8 C_3AH_6	110–130 175–185 280–320

rial from the core. Such an average measurement is insufficient to provide an insight into the progression of the carbonation front.

The experimental procedure described in this paper has been devised to validate a technique for taking several measurements from the same specimen to produce a carbonation profile within a convenient time-frame. This innovative approach provides important information on the shape and progression of the carbonation front, thus allowing conservationists to design mortars for optimum performance within a given context.

Experimental

The length of time taken to run a test is a function of the desired maximum temperature, the heating rate, and the rate at which the machine returns back to the starting temperature. The machine used in these experiments was a refurbished Setaram TG-92 thermogravimetric analyser.

The mass losses for dehydroxylation and decarboxylation are interdependent. The greater percentage of $\text{Ca}(\text{OH})_2$ present, the lower the percentage of CaCO_3 , since the CaCO_3 is formed through the carbonation of the $\text{Ca}(\text{OH})_2$. It is therefore not strictly necessary to measure the decarboxylation since this is known from the measurement of the dehydroxylation. The implication of this is that temperatures need go no higher than 600°C, which reduces both the heating and the cooling times for each testing cycle. A series of experiments was conducted to establish the influence of the rate of heating on the accuracy of the mass loss obtained. It was found that a heating rate of 50°C min^{-1} produced an equally accurate total mass loss as a rate of 10°C min^{-1} .

The materials used are commercially available hydrated CL90 high calcium non-hydraulic lime, and a silica sand with a granulometry (particle size) between 250 and 125 μm . The sand was selected because it is not reactive to TG within the temperature range chosen for the experiments. TG of ~ 50 mg samples contained in alumina crucibles was carried out in flowing, dry air ($16 \text{ cm}^{-3} [\text{STP}] \text{ min}^{-1}$), at a heating rate of $50^\circ\text{C min}^{-1}$, from 60 to 700°C . The start and end temperatures were selected in order to minimise the length of time taken to perform each run. Neither the sand nor the lime are thermally reactive until $\sim 350^\circ\text{C}$. Other aggregates which may be found in mortars can contain impurities or hydrated compounds which are reactive at temperatures $>90^\circ\text{C}$. Even taking account of the potential presence of such materials, it is possible to start the test at 60°C rather than waiting for the machine to return to room temperature (20°C). Compared with techniques requiring purging, more than one atmosphere pressure, and heating rates of only $10^\circ\text{C min}^{-1}$, the time savings for these new tests are of the order of several hours.

Samples were prepared using known masses of lime and sand to a combined mass of ~ 50 mg. The proportions used (by dry material mass) were approximately (lime:sand): 1:0; 1:2; 1:3; 1:4; 1:9; 1:19; 1:39; 0:1.

Results and discussion

Figure 2 is an example plot of original TG data, plus the first derivative of these (referred to as DTG data). The DTG data were calculated using a centred difference numerical differentiation formula.

The dehydroxylation of $\text{Ca}(\text{OH})_2$ is a thermal decomposition process as follows

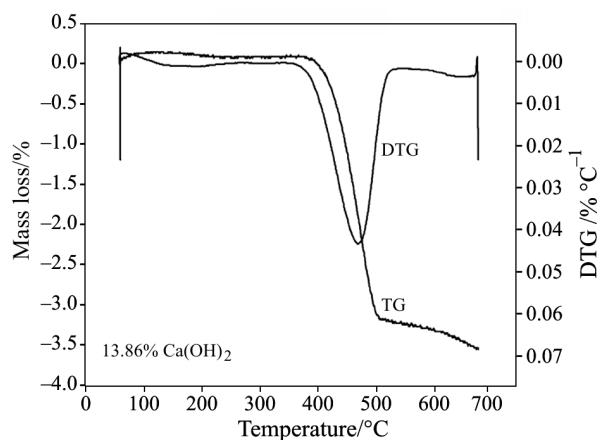
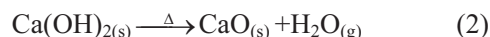


Fig. 2 Thermal analysis of a lime/sand mixture heated at $50^\circ\text{C min}^{-1}$

The measured mass loss during this process is the chemically bound water which is given off as a vapour. Hence the measured mass loss can be used to calculate the mass of $\text{Ca}(\text{OH})_2$ originally present. Thus each mg of mass loss results from the thermal decomposition of $74/18=4.111$ mg of $\text{Ca}(\text{OH})_2$.

Figures 3 and 4 show the TG and DTG curves for each sample, demonstrating the temperature differences in the dehydroxylation start and finish points for different concentrations of lime. The figures given for lime concentrations in these two graphs are from raw data, which have been corrected as follows:

Errors associated with the TG technique

- A blank correction to compensate for the change in mass of air displaced by the sample during heating (buoyancy); this was found to be negligible.

Errors associated with the material

- A correction for adsorbed/absorbed water present in the sample. This can be measured from mass loss up to $\sim 120^\circ\text{C}$ and used to determine 'dry' sample masses.
- A correction applied to the known percentage of lime in each specimen to allow for its equivalent mass of $\text{Ca}(\text{OH})_2$ since CL90 lime is specified as having a minimum of 90% $\text{Ca}(\text{OH})_2$ rather than 100%. In this case the lime was shown by TG to contain 96.69% $\text{Ca}(\text{OH})_2$.

Mass losses during TG of lime/sand mixes are either due to loss of physically adsorbed water or to dehydroxylation. The mass loss due to water evaporation occurs between 60 and $\sim 120^\circ\text{C}$, the mass loss due to dehydroxylation commences at $\sim 350^\circ\text{C}$ and finishes between 500 and 575°C depending on the concentration of lime (Table 1). The DTG curve can be used to identify the temperature at which the mass loss starts

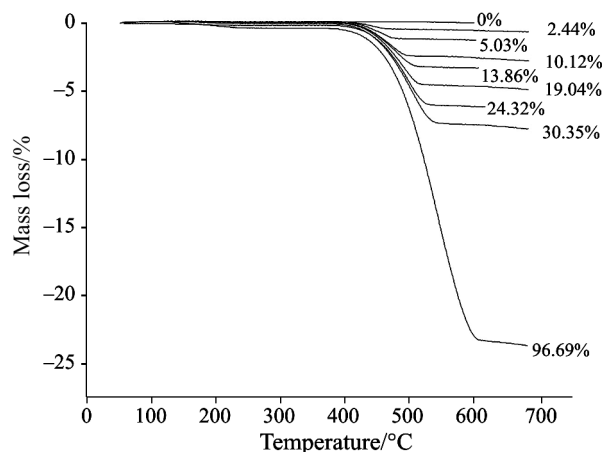
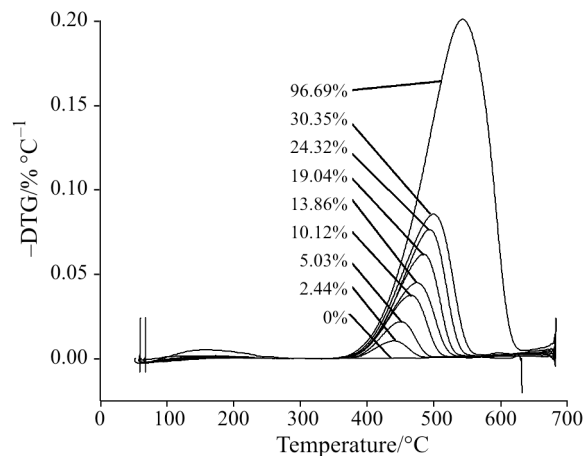


Fig. 3 TG curves for a range of mass concentrations of lime heated at $50^\circ\text{C min}^{-1}$

Table 3 Comparison between measured and expected $\text{Ca}(\text{OH})_2$ content by mass

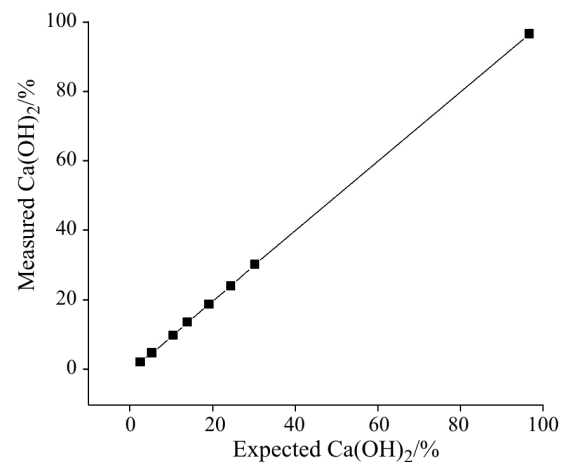
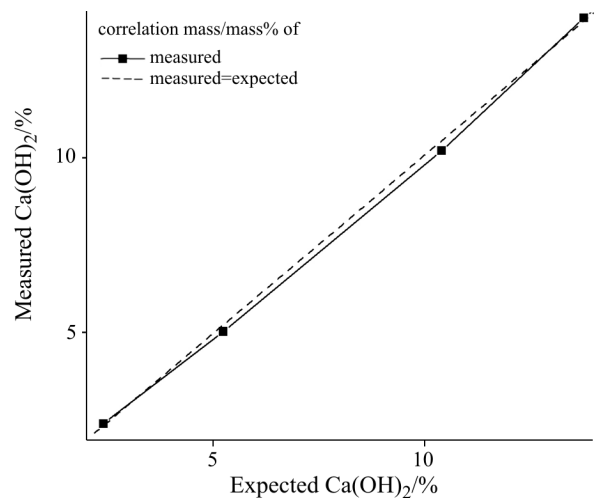
Measured/mass/mass/% $\text{Ca}(\text{OH})_2$	Expected/mass/mass/% $\text{Ca}(\text{OH})_2$	Absolute error/mass/mass/%	Relative error/%
30.18	30.45	-0.27	-0.90
24.34	24.32	0.02	0.06
19.08	19.04	0.04	0.18
13.77	13.86	-0.09	-0.63
10.40	10.12	0.28	2.68
5.22	5.03	0.19	3.71
2.38	2.44	-0.06	-2.36


Fig. 4 DTG curves for a range of mass concentrations of lime heated at $50^\circ\text{C min}^{-1}$

and finishes for the dehydroxylation process with considerable certainty. The actual mass loss between these two temperatures can be measured using the TG curve. This mass loss is then converted into an equivalent mass of $\text{Ca}(\text{OH})_2$ using Eq. (2) above. This equivalent mass of $\text{Ca}(\text{OH})_2$ can then be compared with the known mass of $\text{Ca}(\text{OH})_2$ used in the experiment.

Table 3 and Fig. 5 show the comparison between measured and expected quantities by mass.

The most common B:Ag ratio used for conservation mortars is 1:3 by volume of dry materials. This is equivalent to approximately 1:9 by mass (equivalent to a 10% $\text{Ca}(\text{OH})_2$ concentration) depending on the density of the aggregate. Figure 6 shows the correlation between measured and expected values over the range of 2 to 14%. It can be seen that the correlation is very close over this range, with a slight tendency to underestimate the amount of $\text{Ca}(\text{OH})_2$ present. The absolute errors are below 0.3% in all cases which indicates a small additive error. At the lower concentration levels, this produces a relative error of the order of 3–4%. Given that the mass loss being measured is the chemically bound water, which represents 24% of the $\text{Ca}(\text{OH})_2$ and that this itself represents 2–10% of the total mass of material under test, this is a very low


Fig. 5 Correlation between measured and expected $\text{Ca}(\text{OH})_2$ content by mass

Fig. 6 Correlation between measured and expected $\text{Ca}(\text{OH})_2$ content (mass/mass) over normal range of concentrations

error. However, in order to achieve such accuracy, high resolution TG equipment, such as has been used for these experiments, is required.

Conclusions and further work

The measurement of varying quantities of $\text{Ca}(\text{OH})_2$ present in samples using high speed thermal analysis has been shown to have a very high correlation with known quantities. This demonstrates the practicality of using this technique to measure the amount of $\text{Ca}(\text{OH})_2$ present at different depths within a sample of lime mortar, and hence to follow the carbonation profile as it develops over time.

Further work is in progress on a range of non-hydraulic lime mortars to measure the progress of the carbonation front as it develops over an extended period of time. Sampling is at 3 mm depth increments through the mortar to a depth of 24 mm, and complete profiles are being produced in under 6 h. This work includes mortars containing carbonates and impurities which show thermal decomposition within the range of temperatures being used for these tests. This is being done in order to test out the system with materials which show more complex thermal reactions.

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