



A CRITICAL REVIEW OF TECHNIQUES USED TO ASSESS CARBONATION IN LIME MORTARS*

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Abstract

The carbonation process in high-calcium lime mortars, as well as the chemical, physical and environmental issues involved, are outlined. Literature on carbonation measurement is reviewed and the following techniques are examined: Scanning Electron Microscopy (SEM), Optical Microscopy (OM), Powder X-Ray Diffraction (XRD), Raman Spectroscopy, Differential Thermogravimetric Analysis (DTA), Phenolphthalein staining, Gravimetry, Velocity of the Propagation of Ultrasound Pulses, Elemental Analysis, Drilling Resistance Measurement System (DRMS) and electronic pH measurement. An examination is made of the reasons for which information on carbonation is required, and appropriate techniques for assessing carbonation, based on each reason, are identified. The need for research into the relationship between the evolution of carbonation and the evolution of pore structure is discussed. Preliminary results from research in this area by the author are reported. Tentative proposals are made for an internationally-accepted Standard Protocol.

Keywords

Carbonation, lime-mortar, phenolphthalein, DTA, Raman, SEM.

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1 Introduction

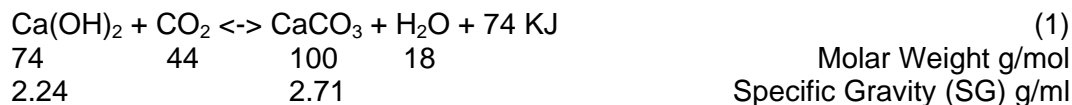
Mortars used for restoration of historic structures are made up of a mixture of a binder and a filler. Typically, the filler is entirely sand, a mixture of sand and crushed stone, or entirely crushed stone. The binder is either hydraulic or non-hydraulic lime, with or without pozzolanic additives or portland cement. Data used in this paper came from tests conducted on a simple form of mortar made up of a non-hydraulic, high-calcium lime binder and a crushed limestone filler.

The first section of the paper describes the carbonation process through the eyes of several researchers who have worked on either cement- or lime-based materials. The process is the same in both binders, and the majority of research has been on cement and concrete carbonation. The next section outlines the techniques used by 26 researchers to measure carbonation between 1981 and 2004 (Table 1). Three novel techniques used by the author - Elemental Analysis, DRMS and electronic pH measurement - are introduced. The various techniques are contrasted and compared. The relationship between carbonation, pore structure and performance is discussed. Finally, some proposals are made on suitable methodologies, which might form part of an internationally-accepted standard.

2 Carbonation

Non-hydraulic high-calcium lime is manufactured by burning a carbonate limestone, which mainly consists of calcium carbonate (CaCO_3), at a temperature of about 900°C to produce calcium oxide (CaO). The calcium oxide is then hydrated in water to form calcium hydroxide (Ca(OH)_2), known as lime. This hydration can be partial, to form dry hydrated lime powder, or complete, to form lime putty. After hydration, the lime putty is sieved and kept in containers under a layer of water. The lime forms a dense slurry, and is generally allowed to mature for a minimum of 3 months before being used. This process ensures that the calcium oxide has been fully converted to calcium hydroxide (portlandite), and that the portlandite crystals are of an even size and distribution throughout the lime putty.

On exposure to air, the lime reacts with carbon dioxide (CO_2) to form calcium carbonate. This process is known as 'carbonation' and is responsible for 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. Ca(OH)_2 makes up a significant proportion of the chemistry of portland cement (OPC). Since the cement industry is several orders of magnitude larger than the lime industry, it is not surprising that research on carbonation is mainly published on cement mortars. Upon hydration, 16 to 20% of OPC is converted to portlandite (Wild & Khatib, 1996), which is the active binder in lime mortar. The subsequent carbonation process is the same in both and much of the research findings are, therefore, transferable from cement to lime. The carbonation process can be described overall by the chemical process (Moorehead, 1986):



The carbonate weighs about 35% more than the hydroxide from which it was formed. There is also an increase in the volume of solids. Ca(OH)_2 (portlandite, which has a SG of 2.24 g/ml and molar volume of 33.0 ml) is converted into CaCO_3 (calcite - or the more unusual crystalline forms vaterite and aragonite - which has a SG of 2.71 g/ml and molar volume 36.9 ml), resulting in an 11.8% increase in the volume of solids. This increase in volume is accommodated by the pores of the mortar and tends to reduce access to CO_2 . The heat generated by the reaction may marginally contribute to evaporation of

water from the pores, which can have the effect of reducing the rate of carbonation, since water is the primary vehicle for carbonation.

Ca(OH)_2 is accessed by the CO_2 in its dissolved state (Johannesson & Utgennant, 2001). There are five stages involved:

1. Diffusion of gaseous CO_2 through the pores of the mortar
2. Dissolution of the CO_2 in the pore water
3. Dissolution of Ca(OH)_2 in the pore water
4. Chemical equilibration of dissolved CO_2 in the pore water
5. Precipitation of CaCO_3

Mathematical models for carbonation have been proposed by Papadakis et al (1991) (cement) and Van Balen & Van Gemert (1994) (lime).

2.1 Diffusion of CO_2 through the mortar

2.1.1 Pore structure

The diffusion of CO_2 through the mortar is controlled by its pore structure, which is influenced by the nature and granulometry of the filler (Houst et al, 1993). In addition, the pore structure is affected by the ongoing carbonation. As CaCO_3 crystals form, they can reduce the size of, or even obstruct, the pores and, thereby, reduce the accessibility of CO_2 to the interior of the material. This results in a reduction in the average pore radius, shifting the pore size distribution at the expense of macropores and in favour of mesopores (Dewaele et al, 1991). The shift in pore size is particularly noticeable in unmodified dispersed hydrated lime mortars, where carbonation can seal the interior from gas percolation (Michnia, 2004).

2.1.2 Relative Humidity

The relative humidity (RH) also has an effect on the diffusion of CO_2 through the pores. As the RH increases, the effective pore radius reduces as a result of the formation of an aqueous film on the walls of the pores. Since diffusion in a liquid is about 10,000 times slower than in air (Houst, 1996), the diffusion of CO_2 is strongly affected by RH. Bentz et al (1995) have shown that when the radius of a pore is smaller than the radius computed from the Kelvin-Laplace equation, capillary condensation will occur. Pore sizes below this critical radius are not, therefore, involved in the carbonation process. At RH levels in excess of 40%, pores with a radius less than 0.4nm become blocked (Houst, 1996), and above 90%, all but the larger macropores will be blocked (Papadakis et al, 1991). Philippi et al (1994) have calculated values for critical radii that range from 5nm at 78.3%RH to 100nm at 99%RH.

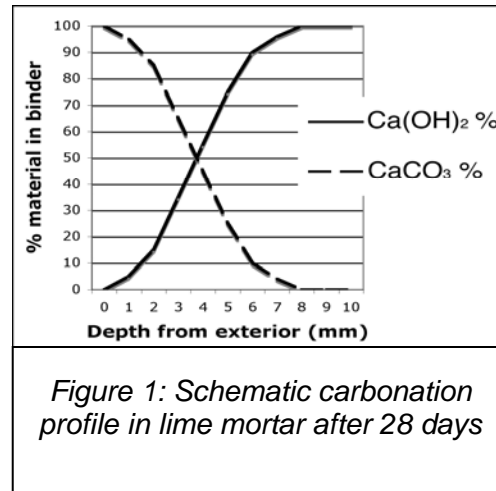
2.1.3 Carbonation process

Moorehead (1986) describes the sequence of chemical reactions that occur as follows: CO_2 dissolves in the pore water to form H^+ , HCO_3^- and CO_3^{2-} ions; Ca(OH)_2 particles dissolve in the reduced pH water to form Ca^{++} ions; these ions react with the CO_3^{2-} ions to form CaCO_3 . This process will continue until either all the Ca(OH)_2 has been converted, or CO_2 is no longer accessible either due to a reduction in relative humidity or as a result of pore blocking by carbonate crystals or excessive moisture content.

2.2 Carbonation Profile

The progression of the so-called 'carbonation front' through the mortar follows the form shown in Figure 1 (Parrott, 1987). There is a transitional zone of mortar at varying carbonation levels between the fully carbonated mortar at the exterior and uncarbonated mortar deeper inside. Since the carbonation process affects the pore structure of the mortar, there is a similar variation in porosity and

pore size distribution along the transitional zone. Moorehead (1986) suggests that the limiting distance for diffusion of CO_2 is 25mm for porous mortars. Because carbonated mortar has higher compressive strength than uncarbonated mortar, there is also an equivalent variation in compressive strength across the profile.



3 Measurement of Carbonation

Techniques for measurement of carbonation can be direct or indirect. Data, illustrations, and graphs shown below are from the author's own work. A summary of tests used by researchers is provided in Table 1.

3.1 Direct methods

3.1.1 Scanning Electron Microscopy (SEM)

SEM offers the opportunity to examine material at far greater magnifications than can be achieved using optical microscopy (OM). The Environmental SEM (ESEM) gives the opportunity for low-vacuum analysis of wet or larger samples, and is suitable for examination of the carbonation front in lime mortar. Individual crystals can be examined (Walker, 1982), as can the bonding between carbonated binder and filler (Lewin, 1981). Pores in the structure, through which CO_2 gains access to uncarbonated $\text{Ca}(\text{OH})_2$, can also be examined. Once a suitable subject has been located in the specimen, ESEM photomicrographs can be rapidly taken for subsequent analysis.

3.1.2 Optical Microscopy (OM)

Crystalline materials can be identified with the use of Polarising and Fluorescent Microscopy (PFM). When a beam of light enters an anisotropic crystal, it is split into two beams of polarised light with different refractive indices. When viewed through a microscope between crossed polars, characteristic interference patterns can be observed, which allow the crystals to be identified. In addition, voids can be seen and counted if the specimen is impregnated with a fluorescent resin. This procedure gives insight into the pore structure (Brocken et al, 1999; Leslie & Hughes, 2002). Preparation of slides is time consuming and problematic for friable materials, such as lime mortars. However, once prepared, they can be quickly examined, photographed and analysed.

(Brocken et al, 1999). In general, researchers use XRD to detect the presence of a certain material, rather than the quantity of that material (for example Lanas & Alvarez, 2003). As can be seen from Figure 2, signatures of the constituent materials are confused by noise, increasing the difficulty of extracting quantitative data. For powder XRD, samples need to be very finely ground, and tests take several hours to perform.

3.1.4 Raman Spectroscopy

The Raman effect was discovered in 1928 and has been used to characterise material ever since. Only recently has the technique been applied to lime mortars (Martinez-Ramirez et al, 2003). There is a general carbonate peak at 1085 cm^{-1} that clearly identifies the presence of CaCO_3 . Calcite, vaterite, and aragonite signals overlap closely at this vibrational mode, but they all have distinctive spectra in the $700 - 800\text{ cm}^{-1}$ region that allow the forms to be differentiated. Ca(OH)_2 produces a strong peak at 3620 and 3640 cm^{-1} (Dawson et al, 1973). Figure 3 shows the Raman frequencies for a 7-day-old lime mortar made with crushed limestone filler. Note the strong signal at 3620 cm^{-1} , characteristic of Ca(OH)_2 , and the signal at 1085 cm^{-1} from the limestone filler. Background fluorescence from impurities in the filler has been found to be a severe problem with some samples, much as it is with XRD. UV lasers produce significantly less fluorescence. The author is working with others to develop methodologies to take advantage of the promising results from Raman spectroscopy. Testing can be done on either crushed material or a prepared surface, and only takes a few minutes.

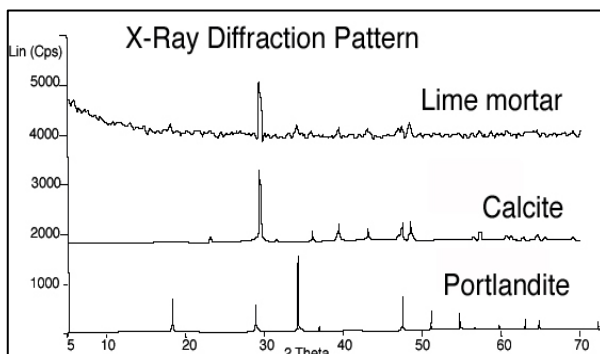


Figure 2: XRD pattern for Lime mortar, Calcite (The major crystalline form of CaCO_3), & Portlandite (Ca(OH)_2)

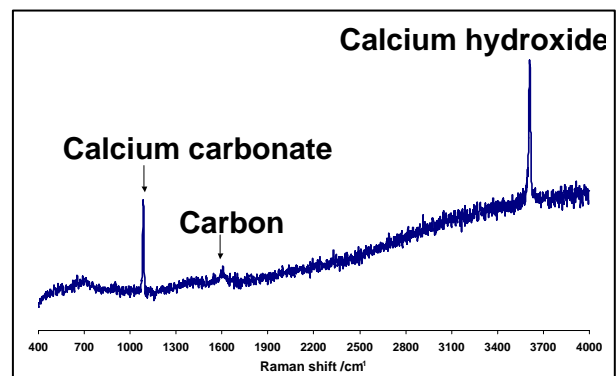


Figure 3: Raman spectra for 7-day-old lime mortar (Raman shift vs intensity)

3.1.5 Thermogravimetry

Differential Thermogravimetric Analysis (DTA) is a powerful tool that is much used for the analysis of cements and mortars, as can be seen from Table 1. Figure 4 shows the DTA results for a sample contained in an alumina crucible and heated from room temperature to 1000°C at $10^\circ\text{C min}^{-1}$ in flowing dry air in a Setaram TG-92 thermogravimetric analyser. The major and clearly differentiated weight losses occur at around 450°C [conversion of Ca(OH)_2 to CaO – dehydroxylation] and 800°C (conversion of CaCO_3 to CaO – decarbonation) The areas described by the curves can be used to calculate the weight of water and carbon-dioxide lost and, hence, the relative proportions of Ca(OH)_2 and CaCO_3 can be accurately calculated. The shape of the decarbonation curve can also be used to identify different crystalline forms of CaCO_3 – amorphous carbonate, calcite, aragonite & vaterite (Moorhead, 1986). Testing is performed on about 100 mg of material and takes 2 to 3 hours to perform.

3.2 Indirect Methods

3.2.1 Alkalinity Indicators

Since $\text{Ca}(\text{OH})_2$ is highly alkaline (pH 12), a standard method of identifying its known presence is with the use of alkalinity indicators (RILEM, 1998). The most commonly-used indicator is phenolphthalein, which changes from colourless to a strong red above about pH 9.0 (Figure 5). This pH level does not correspond to either the boundary between fully-carbonated and partially-carbonated mortar, or between partially-carbonated and uncarbonated mortar (Houst et al, 2002). Parrott (1990) used additional indicators on powder obtained from different drill depths to obtain an alkalinity (and hence carbonation) profile in concrete. The author has not found any researcher of lime mortars who has used this extended technique, although most researchers use phenolphthalein (Table 1). Testing is quick and cheap, but some indicators require careful use as colour changes can be quite subtle.

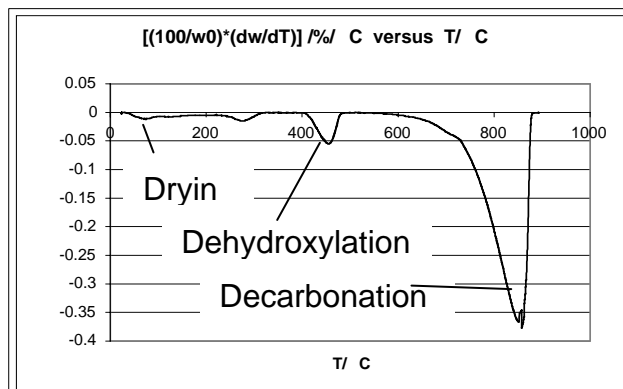


Figure 4: DTA curve for 28 day lime mortar

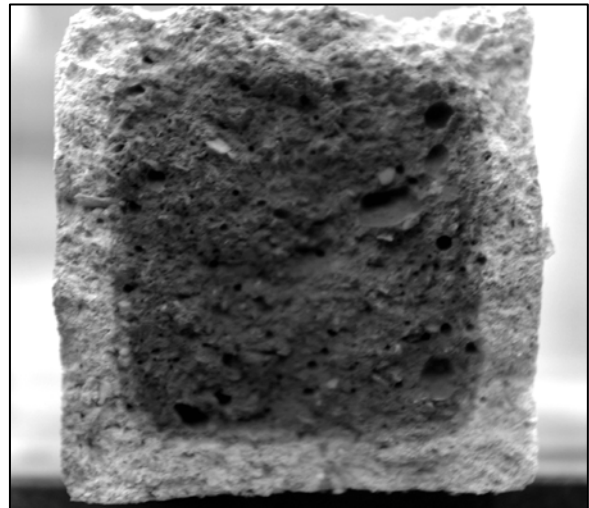


Figure 5 Phenolphthalein staining on a 28 day old specimen

3.2.2 Gravimetry

As can be seen from equation (1) above, mortar gains weight as it carbonates. Medici & Rinaldi (2002) used gravimetry to establish the weight of CaCO_3 that has formed at a particular point in time. This technique requires the use of micro-balances in an enclosed controlled atmosphere and is generally used with small cement or lime paste samples.

3.2.3 Velocity of Ultra-sound

This non-destructive technique has been pioneered by Cazalla et al (1999, 2000). The carbonation process is characterised by an increase in the velocity of longitudinal ultrasonic waves and is related to the degree of compactness. The greater the longitudinal velocity, the greater the decrease in the total anisotropy of the samples. Analysis of the data uses analysis of variance (ANOVA) models. The advantage of this method is that it is non-destructive, and a large number of measurements can be taken rapidly. This technique does not give absolute data, but rather gives a measurement of the changes in mechanical properties taking place within the mortar. Cazalla offers this technique as a quick and inexpensive, non-destructive method of comparing the performance of different materials.

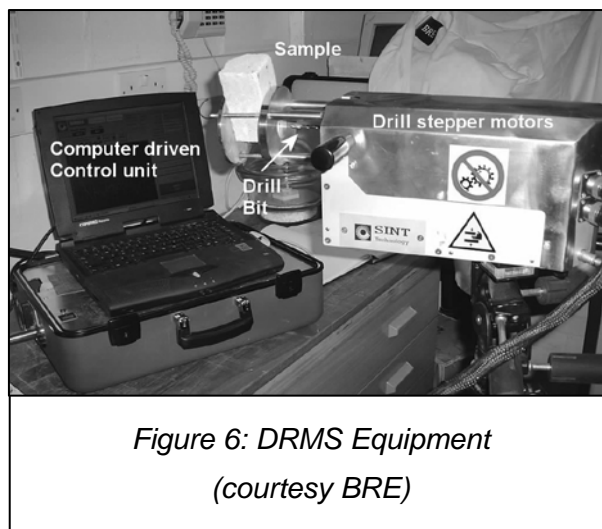
3.3 Novel techniques

3.3.1 Elemental Analysis

Automatic determination of carbon, hydrogen and nitrogen has been performed since the 1960s using Perkin-Elmer analysers for organic elemental microanalysis (Belcher, 1977). As far as the author is aware, it has never been used to analyse lime mortars. The chemical formulation of lime is ideally suited to elemental analysis since hydrogen is not present in CaCO_3 and carbon is not present in Ca(OH)_2 . In the case of a non-hydraulic lime mortar (assuming the aggregate does not contain any carbon), any carbon found has to be the result of carbonation. In circumstances where aggregates contain limestone or calcitic sandstone, a baseline measurement on uncarbonated mortar can be taken, and subsequent increases in carbon content can be assumed to be the result of carbonation. This technique uses small quantities of material and the test only takes 5 minutes to perform. Results are given as percentages by weight of carbon, hydrogen and nitrogen present in the sample. Care needs to be taken in interpreting the results, because hydrogen is also present in water. Since dried crushed mortar is hygroscopic, a proportion of the hydrogen that is found will not relate to the presence of hydroxides.

3.3.2 Drilling Resistance Measurement System

The Drilling Resistance Measurement System (DRMS) (Figure 6) is designed to measure the force required to drill a hole at constant rotation (rpm) and lateral feed rate (mm/min). The force is known to correlate with the compressive strength of the material. When the rotation, lateral feed rate and type of drill bit are held constant, the measured force is an indication of the strength of the material. Since the compressive strength of mortar varies according to the extent of carbonation, this system can be used to map changes in compressive strength and, hence, changes in carbonation across the carbonation front. A standard exists for cement mortar, which can be adapted for lime mortar given suitable testing. (RILEM, 2004) The author is currently experimenting with the use of this technology.



3.3.3 PH measurement using pH meter

The difficulty in reading colour changes in pH indicators can theoretically be overcome by the use of pH meters. The author is currently experimenting with a suspension of crushed material in distilled water in order to develop a satisfactory protocol. The results show the potential of producing comparable data to that of elemental analysis, with the additional benefit of being cheaper and usable

in the field. Although not investigating carbonation, Shirakawa et al (1999) have shown that variations in pH of lime mortar can be measured using pH meters. They placed 3mm-thick specimens of lime mortar in distilled water for 2 days before measuring the resultant pH. The results showed good reproducibility with low standard deviations.

Discussion

3.4 Research approaches

3.4.1 Carbonation in Cement

Research into carbonation of cement, in the majority of cases, makes use of alkalinity indicators and TG (Table 1). Since carbonation is viewed as a 'problem' (Papadakis, 1991) that encourages corrosion in underlying reinforcement, the focus has been on measuring the depth of carbonation. Techniques used have, therefore, been those that best provide such information. The most sophisticated of these techniques is that developed by Parrott (1990), where a 20mm-diameter drill extracted material in 2.5mm-stages to a depth of 35mm. At each stage, the extracted powder was tested with 11 different indicator solutions to give a pH profile and by TG to give a $\text{Ca}(\text{OH})_2 / \text{CaCO}_3$ profile.

3.4.2 Research into Lime mortars

Carbonation in lime mortars, rather than being a problem, is the 'active ingredient' that transforms the mortar into a structurally stable and competent building material. A great deal of research has been undertaken into the characterisation of historic mortars (Bartos et al, 2000). This research makes use of a wide variety of techniques including XRD, TG, SEM, PFM, Fourier Transform Infra-Red Spectroscopy (FTIR) and Wet Chemical Analysis (Middendorf et al, 2000). As can be seen in Table 1, many of these techniques have also been used on new mortars.

3.4.2.1 Research with little reference to carbonation

Conservation repair mortars have frequently been designed to replicate historic mortars (Leslie & Gibbons, 2000). The design of such mortars often concentrates on the desirable physical characteristics (Peroni et al, 1981; Henriques & Chaola, 1996; Charola & Henriques, 1999), with only a passing reference to carbonation. Similarly, some studies on the evolution of mechanical properties of lime mortars, such as Bromblet, (2000), do not attempt any measurement of carbonation.

3.4.2.2 Research with little quantification of carbonation

Lanas & Alvarez (2003) used XRD and TG to follow the progress of carbonation. They report the results as a percentage of the whole, with samples being taken from the core and the edges '*to avoid differences in the carbonation depth*'. Cazalla et al (1999) used ultrasonic testing to evaluate the degree of carbonation. Cazalla et al (2000) used phenolphthalein for qualitative evaluation and XRD analysis to evaluate the relative proportions of calcite and portlandite over time at the core and at the edge of the samples. Velosa & Veiga (2004) used phenolphthalein to evaluate the percentage degree of carbonation. Qualitative evaluation of carbonation by phenolphthalein staining is used by Peroni et al (1981) and Elert et al (2002).

3.4.2.3 Research with quantification of carbonation

Where quantification of carbonation has been attempted, reliance has been on phenolphthalein staining and results are given in terms of the depth of carbonation. Both Ashall & Butlin (1996) and Baronio et al (2000) measure the depth, but do not report the results except in comparative terms. Stewart et al (2001) use the RILEM standard (RILEM, 1998) and quote carbonation depths achieved at the end of their study.

3.4.2.4 Theoretical research

Whilst Moorehead (1986) and Parrott (1990) have described the chemical and physical processes of carbonation, Papadakis et al (1991) and Van Balen & Van Gemert (1994) have proposed mathematical models for carbonation. The former model is based on concrete carbonation, and the latter on lime mortar. The Van Balen & Van Gemert model expresses carbonation in the form of a differential equation with a 'sink' term that is based on concentrations of lime and of CO₂. Since carbonation is governed by access to CO₂, which in turn is controlled by the structure of the mortar, a diffusion coefficient is also involved. The final factor is an equation to describe water vapour transport as the whole system dries out. One assumption made in this model is that the diffusion coefficient is more or less constant. This assumption ignores the pore size and distribution changes that occur during carbonation.

3.5 Relationship between carbonation, pore structure and mortar performance

In a high-calcium lime mortar, the changes in structure and in mechanical properties are entirely a function of carbonation. Both the carbonation process and the method by which the pore structure of the mortar is affected must be understood. Because cement has a tighter pore structure than lime mortar, small changes in the structure can have larger impact on the water and gas transport in cement than in lime mortar. Changes in the pore structure change the progress of carbonation (Moorehead on cement, 1986), and also have an effect on mechanical strength (Lanas & Alvarez on lime, 2003). The pore structure of the mortar controls its water transport characteristics, which strongly affect durability and resistance to agents of decay (Ginell on porous materials, 1994). Changes in pore structure caused by carbonation include a significant reduction in total porosity (Houst on cement, 1996), and permeability reductions between 3 and 5 orders of magnitude (Dewaele et al on cement, 1991). Cazalla et al (on lime, 2002) associate reduction of porosity values with higher degrees of carbonation.

More research into this relationship is required, as there is some disagreement amongst researchers. For example, Thomas et al (on cement, 1996) report a significant reduction in BET surface area, but Johannesson & Utgenannt (on cement, 2001) conclude that the change is only on the order of 10%. Techniques for examining pore structure include nitrogen adsorption, mercury intrusion porosimetry (MIP), SEM, and OM (on an increasing scale from micropores to macropores). There has been some debate on the validity of using MIP in cement-based materials. Indeed, Diamond (on cement, 2000) states that it is wholly inappropriate, although he drew this conclusion after having conducted only the most basic of porosimetry experiments. Portsmouth & Gladden (1992) have shown that use of the mercury extrusion curve will give the size of pores shielded by narrow entrance necks if analysed using the right equation. Philippi et al (on lime, 1994) used SEM to obtain pore size distributions for pore sizes greater than 125 nm, and adsorption isotherms below that size. Papayianni & Stefanidou (on lime, 2001) used MIP, as did Lanas & Alvarez (on lime) (2003) and (2004).

3.6 Significance of measurement of depth of carbonation

Characterisation of lime mortars is an important aspect of conservation of historic structures. Much work has been concentrated on analysis of historic mortars (Bartos et al, 2000) in order to be able to respect original construction techniques. Many of these analytical techniques, whilst effective for the characterisation of mortars, have been used on new conservation mortars in ways that are not always appropriate. Since lime mortars carbonate from the outside inward, consideration of the *depth* of carbonation, rather than the *percentage* of carbonation, is much more useful. The depth of carbonation is independent of the dimensions of the mortar. Therefore, information on the percentage of carbonation can be misleading, as this relates as much to the dimensions of the specimen as to the

constituent parts of the mortar. Analysis of depth of carbonation data is readily transferable to practice, in the design of the mortar as well as the size and dimensions of the repair.

3.7 Techniques for quantification of the depth of carbonation

Where quantification of carbonation has been attempted, the following techniques have been used:

- Velocity of ultra-sound
- X-Ray Diffraction
- Measurement of the depth of phenolphthalein (or other indicator) staining
- Thermogravimetry

The use of ultrasound can only produce information on changes over time. XRD analysis is difficult to quantify, and is subject to noise. The use of indicator staining is complex and some indicators are difficult to read. Phenolphthalein used on its own will not delineate either the start or the end of the carbonation front. The data is, therefore, difficult to analyse. However, it is a quick and cheap method of getting a broad impression of the extent of carbonation. The potential shown by the use of pH meters is worthy of further development, since they are also cheap and portable, and can theoretically describe the entire carbonation front.

Thermogravimetry is sensitive and accurate. If samples are taken at regular depth intervals, TG is able to give a clear, reproducible profile. Sensitive TG equipment is expensive, and tests take several hours to conduct. The testing of one profile of 10 points might take three or four days to complete. The author is examining the efficacy of increasing the rate of heating, and only measuring the dehydroxylation, which occurs below 500°C, thus saving 50% of the heating time. If successful, this could enable production of a complete profile in one day. The quality of data would suffer, particularly in the loss of data on subtle differences to the decarbonation curve, but the profile would still be valid. Elemental analysis does not give the same quality of information as TG, but the data produced should give a quick and accurate carbonation profile, although more work needs to be done to validate the technique.

The use of DRMS is interesting. The data produced is continuous in nature and takes a few minutes to produce. Although it is an indirect method of measuring compressive strength, the method is well proven and data can be related to strength gains produced by carbonation. As with ultrasound, the data is relative rather than absolute, but the quality is detailed enough to reveal the shape of the carbonation front. The technique directly accesses and quantifies the strength gain produced by carbonation. In circumstances where destructive testing is acceptable, DRMS will produce better quality of data than ultrasound. As with elemental analysis, more work needs to be done to validate the technique in the context of carbonation measurement.

Raman spectroscopy also shows promise for mapping the carbonation front, provided that the fluorescence produced by the filler can be minimized. Analysis of carbonation is more suited to Raman than to XRD in terms of the ease of differentiating the data produced. Quantification is similarly problematic, but the potential to use a whole sample (as compared to crushed material) gives the possibility of following the carbonation front through a series of measurements on one specimen.

3.8 Practical Issues

3.8.1 Sample storage

Although the rate of carbonation is comparatively slow in a lime mortar, access to CO₂ is greatly increased once a sample is taken and crushed for analysis. Unless testing is performed within 24 hours, samples will no longer be truly representative of the original specimen. Thomas et al (1996) have shown that storage of material in nitrogen in sealed glass containers (CO₂ penetrates plastic

vials) will arrest carbonation for at least 41 days. Therefore, material can be stored for a limited period of time prior to testing if necessary due to machine failure or temporary unavailability of a particular test.

3.8.2 Dessication

The standard method of sample preparation is to dry the material in an oven at 105°C until no further weight loss is measured. When samples are intended to be tested for pore structure, this method of preparation is inappropriate. Malaga et al (2004) has shown that calcitic matrices suffer granular decohesion that results in increased porosity when exposed to temperatures in excess of 50°C. Samples should, therefore, be dessicated at temperatures below 50°C.

4 Recommendations

In order to compare the results from different researchers, a mutually-agreed-upon set of experimental techniques is required. Henriques & Charola (1996) and Charola & Henriques (1999) propose a range of standard tests to be used on lime mortars, but carbonation is not included in their recommendations. The author proposes that testing for carbonation should be added to these standard tests, and that the testing should address the following :

- Techniques that measure the *depth* of carbonation should be used
- Extent of carbonation should be reported in terms of penetration depth
- The shape of the carbonation front should be evaluated
- The impact of carbonation on the pore structure of the material should be evaluated

At present, the most appropriate method for measuring the depth and progression of carbonation would seem to be thermogravimetry. Until alternative methods are validated, thermogravimetric measurement of samples at 2mm depth increments should be used as the standard method of measuring the depth and profile of the carbonation front in lime mortars.

Much of the work on cement and concrete can be built upon to transfer techniques, where appropriate, to lime mortars. There is a need for more research into carbonation of lime mortars. The research should include methods of measurement, the relationship between carbonation and pore structure, and the shape of the carbonation front. Information in these areas will advance knowledge on the comparative performance of different mortar formulations.

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