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Carbonation reaction of lime, kinetics at ambient temperature

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Abstract

The uptake of carbon dioxide due to the carbonation reaction of $Ca(OH)_2$ in ambient temperature of approximately 20 °C has been studied. Different types of lime have been used and the CO_2 concentration has been varied to identify the influence of different variables on the kinetics of the reaction. A closed loop system has been developed and validated that allows measurement of the carbonation progress directly from monitoring CO_2 uptake. Thermal analysis (TA) was used to verify the degree of carbonation that reached up to 83%. Factor analysis on the data set has demonstrated that reaction speed is not dependent upon the CO_2 concentration within the limits tested. Carbonation speed depends on the specific surface of the lime. The results of this study contribute to research carried out on lime mortar carbonation models and on the carbonation process in general.

Keywords: Reaction; Kinetics; Carbonation; $Ca(OH)_2$; $CaCO_3$; Mortar

1. Introduction

Lime has long been used as a binder in mortars. The hardening of lime due to carbonation is responsible for the increase of strength of the mortar and for the modifications of its porous system. Little research has been carried out to model the carbonation process in porous materials such as lime mortars [1] or to study the effect of the carbonation process on lime mortar properties [2,3]. Researchers in different scientific fields have reported on the carbonation of lime as a chemical reaction process [4,5]. Research on carbonation has also focused on the carbonation of cement-based materials such as concrete [6–16] or cement-based waste deposits [17] considering its long-term behavior [18,19]. Research on chemical water treatment has also contributed to the modeling of the reaction between lime and water [4,20]. Research on gas treatment such as desulphurization [5] has dealt with the reaction of gaseous phases with lime.

Lime mortar carbonation is controlled by two mechanisms: carbon dioxide diffusion from the air through the porous system up to the reaction front and the reaction of the diffused carbon dioxide with $Ca(OH)_2$. Both have been integrated in a lime mortar carbonation model developed in the early nineties [1]. Some data used to develop the lime mortar carbonation model were taken from the literature from various research areas. Meanwhile, experimental results give more reliable data to be integrated in the carbonation model. In first instance, an update is given on the influence of the presence of water on the diffusion of carbon dioxide in a porous lime mortar. The second and main contribution of this article is on the study of the parameters influencing the reaction of lime with carbon dioxide. The experimental results of a set-up measuring the uptake of carbon dioxide by lime hydrate are presented. From those results, the influence of the carbon dioxide concentration and some of the material properties on the carbonation reaction is defined.

1.1. Carbon dioxide diffusion through porous lime mortar

The diffusivity of mortar for gaseous carbon dioxide in air depends on the openness of the porous structure and thus on the presence of water in the pores. Diffusion of CO_2 in water is approximately 10000 times lower than in air [21,22], therefore almost excluding it as a transfer mechanism to bring CO_2 to the reaction front.

As water is present in the initial phase of the mortar hardening and as water is released due to the carbonation

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reaction, diffusion resistance will depend on the drying rate of the mortar as well as on the speed of water production due to carbonation. The latter will only become crucial when the carbonation is accelerated at elevated carbon dioxide concentrations.

In Ref. [1], the interdependence between water content and the progress of lime mortar carbonation has been reported. In this contribution, the relation between water content and the effective carbon dioxide diffusion coefficient (D_{effc}) has been extrapolated from isotherms. It seemed acceptable to estimate that the coefficient would drop 100 times when the equilibrium water content of the mortar at 100% RH was reached, approximating the critical water content of the material (53.4 kg/m^3). This assumption resulted in the following relationship between the effective diffusion coefficient and the water content of lime mortar, in which D_{effc} has a maximum value for a dry material and is asymptotic to 0 at the critical water content.

$$D_{\text{effc}} = \frac{1}{5.26 \times 10^6 + 5.21 \times 10^6 (w/53.4)^{12}} \tag{1}$$

In Ref. [23], an update was given of this relation based on measurements. An experimental set-up with a diffusion chamber allowed the measurement of the CO_2 diffusion coefficient of lime mortar (D_{effc} [m^2/s]) at different water contents (w [kg/m^3]). Those results showed that the diffusion coefficient decreases almost linearly between the dry mortar and the capillary water content (248 kg/m^3) (Fig. 1).

This seems to indicate that when a porous material is drying, up to the capillary water content—this corresponds with the end of capillary water flow—the water system is continuous enough to hinder gaseous carbon dioxide diffusion. When the material further dries, the diffusion coefficient increases steadily until reaching the diffusion coefficient related to the nature of the porous system of the completely dry material.

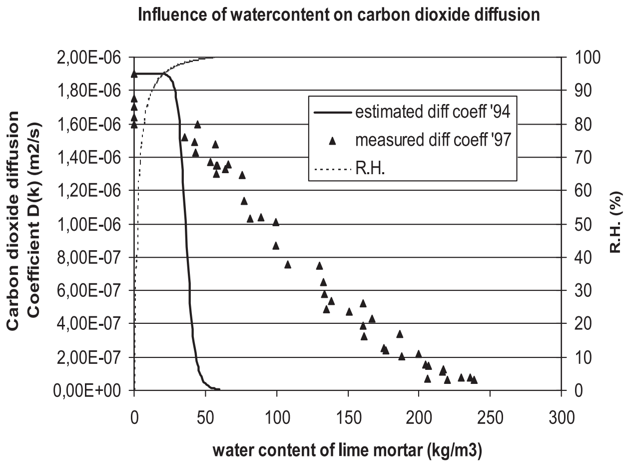

Fig. 1. Updated relation between carbon dioxide diffusion coefficient (m^2/s) and water content (kg/m^3) of lime mortar; the curve "measured …'97" represents the updated data [23] of the trend "estimated …94" in Ref. [1], curve RH gives the relation between the equilibrium water content (kg/m^3) at RH (%).

Through the test data, a curve of the same type as in Eq. (1) was fitted, passing through the same diffusion coefficient value of the dry lime at $w = 0$ and approaching 0 at the capillary water content. The formulation of the fitted curve is given in Eq. (2)

$$D_{\text{effc}} = \frac{1}{5.26 \times 10^6 + 8.73 \times 10^6 (w/248)^3} \tag{2}$$

This formulation has a very high correlation with the measured data (R^2=.98). The mathematical formulation allows for a maximum value for the dry material and a value that is asymptotic to 0 at high water content above capillary water content. Such formulation is more continuous than a linear expression that would include discontinuities at $w = 0$ and $w = w_{\text{cap}}$.

1.2. Carbonation reaction in lime mortar

The carbonation reaction described in Ref. [1] is based on the literature data mainly derived from chemical water treatment applications.

In the differential equation that describes the carbonation process (Eq. (3)), the following terms can be identified. A term for the diffusion of carbon dioxide through the porous system and a term to take into account for the change of concentration (c) due to uptake of carbon dioxide into the porosity (ψ). Finally, the reaction term or sink term $R(w,c)$ that expresses the carbonation reaction that is depending on the carbon dioxide concentration (c) and the water content (w).

$$\text{div}(D_{\text{effc}} \Delta c) + \psi \frac{dc}{dt} + R(w,c) = 0 \tag{3}$$

The reaction term defines that in an elementary volume dx × dy × dz, R moles of gas per unit of time and unit of mortar volume is consumed by the reaction; consequently, the same mole of $Ca(OH)_2$ is converted into $CaCO_3$. The reaction term is calculated for the type of lime mortar under investigation. In the model, all lime is accessible to carbon dioxide as it is concentrated at the pore surface. Water available for dissolution of lime and CO_2 is modeled on that surface. Based on a specific surface of the lime mortar pore system ($A = 3.953\ 10^6$ m^2/m^3), the estimated amount of water with a thickness of five molecular layers could be identified and hence the reaction term in isothermal conditions could be calculated as:

$$R = .7062[CO_2]\alpha(\text{RH})\beta([Ca(OH)_2]) \tag{4}$$

A relation for α(RH) including the influence of RH on the reaction term is proposed while $\beta([Ca(OH)_2])$ could be calculated at every time step as the ratio of the pore surface taken in by the remaining amount of lime over the initial total pore surface. As all lime was assumed to be on the pore surface the ratio corresponds with the still available amount of lime $[Ca(OH)_2]$ over the initial amount of lime per volume unit ($[Ca(OH)_2]_o = 3000$ mol/m^3).

The diffusion model and the reaction model are combined and simulations have been carried out. They allowed simulating accelerated carbonation processes, pointing towards the hindering effect that normal drying conditions could have on the progress of carbonation [1]. An explanation is given for some (historic) cases described in the literature on the optimum conditions for accelerated carbonation of lime based building units [24,25] or lime mortar [26]. An explanation could also be given for the inaccuracy that rises from using weight to identify the progress of a carbonation process [27].

In the abovementioned model, the reaction term $R(w,c)$ has been defined based on the literature from water treatment. The next step in the research is to verify these models in conditions relevant to the carbonation of lime. Such verification could only be done carrying out experiments using a reliable set-up. Such experiments should allow verifying if the reaction speed is also proportional to the carbon dioxide concentration in case of mortar carbonation. They should also aim at defining the lime properties that influence the reaction speed.

2. Set-up measuring lime carbonation reaction

To improve the modeling of the carbonation reaction, a new experimental set-up has been made that is able to measure carbon dioxide uptake directly. This should avoid possible errors using weight gain as a measure for carbonation process as has been shown by [27]. Nevertheless, some researchers [5] have used that procedure in conditions where drying can be assumed to be faster—due to higher temperature and higher gas flow—than in those that will be used hereafter.

2.1. Principles

The carbonation set-up consists of a close loop in which a mixture of air and carbon dioxide could be introduced at a certain RH. A sample holder containing a lime sample can be introduced into the loop through a set of valves. Due to the carbonation reaction, an amount of CO_2 molecules will be immobilized reducing the concentration of carbon dioxide in the circulating gas mixture. The CO_2 concentration in the gas is measured using an IR absorption device. A pump is used to circulate the gas while also temperature and RH are measured.

As the IR absorption device to measure the carbon dioxide concentration should be protected from internal condensation, introducing a water absorber or cooler was considered. As such features could also act as ‘‘sinks’’ for carbon dioxide that could lead to a wrong estimate of the amount of carbon dioxide taken up by the carbonation, experimental conditions have been designed to avoid condensation while measuring RH into the system.

Previous attempts with a similar set-up have been carried out at our institute in 1999. In the unpublished master thesis [28], the results are reported of a set-up that was designed in an attempt to measure the reaction speed between lime and carbon dioxide. Carbonation tests were carried out in a very similar set-up as the one that will be described later in more details. There were however differences. In the previous experiment,

1. a reservoir of silica-gel was placed into the loop between the sample and the IR carbon dioxide instrument to protect it against high humidity (according to specifications of the manufacturer;
2. rehumidification after passing the instrument was accomplished by bubbling the gas through a water reservoir before reaching the sample again;
3. the lime sample for the carbonation experiment was approximately 1 g (1/74 mol) of lime hydrate, humidified but still in powder. Long-term slaked lime putties were also dried.

Tests aimed at defining the initial rate of carbon dioxide uptake. Tests were running for approximately 24 h and stopped before full carbonation was achieved.

The difference in assumed amount of carbonated lime (calcite) from the carbonation test and the results from chemical analysis on the samples as well as from thermal analysis (TA) carried out at the Getty Conservation Institute in Los Angeles (USA) led to some doubts on those first results. The carbonation experiment assumed a much higher degree of carbonation than was identified by the TA.

2.2. Set-up description

Recently, a new set-up has been designed and made. The set-up was scaled down from a total internal volume of approximately 21 to approximately 1.2 l, sample size was reduced, and working conditions were reviewed to avoid condensation without drying and rewetting phases. Dry samples were replaced by small samples of lime putty. Monitoring of the variables of the process was improved.

The set-up scheme is given in Fig. 2. The numbers in the figure refer to the list of the components given here.

The components are as follows:

1. A buffer gas volume, approximately 1 l; a water flow through the double walls linked with a thermal bath is

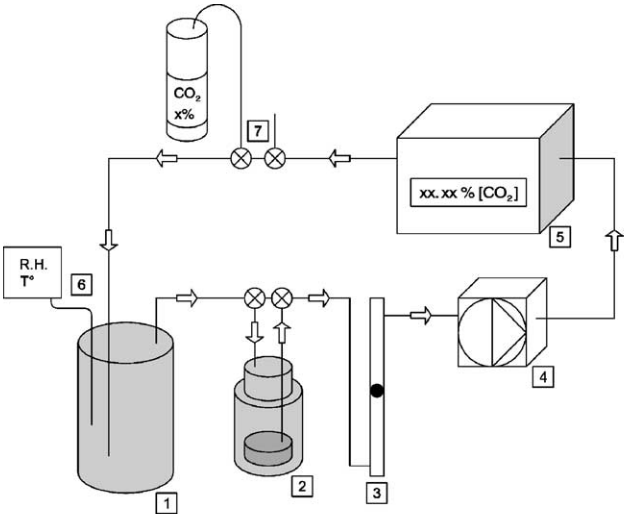

Fig. 2. Schematic representation of the experimental set-up.

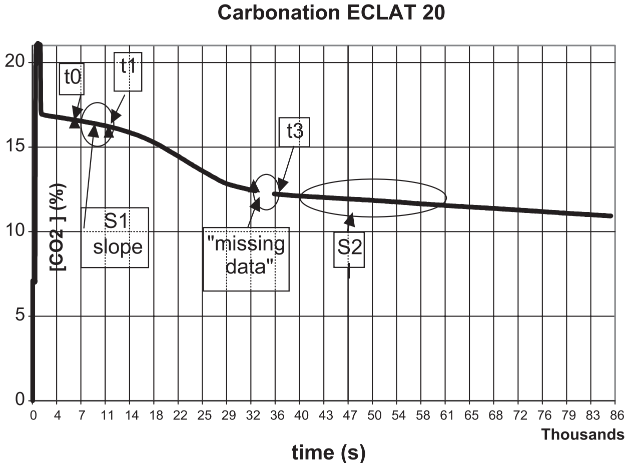

Fig. 3. Example of the collected data from the IR device featuring also the identification of the position of t_0, t_1, and t_2 and the slopes S_1 and S_2. t_0 is the start of the experiment after equilibrium of the set-up is reached, t_1 is the start, and t_2 the end of the increased uptake due to carbonation.

keeping the buffer at a constant temperature; the total volume of the loop (buffer, tubing, and pump) without sample holder is 1.182 l.

2. Sample holder of 0.329 l; the sample holder can be connected through two valves that deviate the airflow through the sample holder when measurements start. The volume of the whole set-up with sample holder in line is 1.512 l.
3. Flow meter with a valve to set the flow speed (Cole Palmer, flow set at approximately 1.5 l/min).
4. Hermetically sealed pump.
5. ABB Advance Optima Easyline IR [CO_2] measuring device (0–100%).
6. Rotronic Hygroflex device to measure RH and temperature from a measuring cell in one (second in the direction of the flow) of the buffer volumes.
7. Valves to control the direction of the flow, allowing to "fill" the set-up with a humidified standard gas (20% or 50% [CO_2] according to the start concentration wanted) before the sample holder (with the sample) is connected to the loop.

Due to the set-up, gas compression and expansion are occurring between the pump and the flow meter/controller so that condensation of water may occur in the tubing when the set-up is not properly dried between each test. Local condensation in the tubes however protected the IR [CO_2] measuring device against internal condensation.

The samples of lime putty (varying between 0.09 and 1 g, most weighing approximately 0.35 g) were spread thinly over a plastic sample cup to avoid as much as possible diffusion resistance in the mass of the sample. The cup with the sample was then introduced in the sample holder. Thanks to this procedure, an accurate mass of lime could be introduced in the experimental set-up and the mass of the sample after the experiment could be measured. The carbonated samples were stored in a closed reservoir to prevent further carbonation until they were subjected to TA to verify the amount of lime that had carbonated. TA was performed on a Mettler Toledo TGA/SDTA 851e.

Raw data collected from the set-up include time (s) and [CO_2] (%), and at distinct moments RH (%) and temperature (°C) are manually introduced in a spreadsheet. Typically, data from the ABB Advance Optima Easyline IR [CO_2] are automatically collected every 100 s. Carbon dioxide concentration [CO_2] (%) was given with two decimals; RH (%) with one decimal and time is given in units of seconds. A graphical representation of those data is given in Fig. 3. As the information density is high, smoothing is required; therefore, a 5-min average on the speed data was calculated (see Fig. 4).

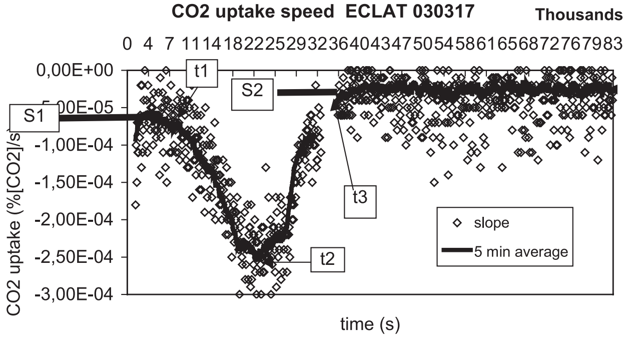

Fig. 4. The derivatives of the CO_2 concentration (dots) are smoothed to 5 min averages (thick line) that clearly reveal the trend. To be able to relate the uptake speed at the [CO_2] at that specific moment with the [CO_2]t_1 at the start of carbonation (t_1). The positions of t_1, t_2, and t_2 are given, the slopes S_1 and S_2 are here represented as constant values.

2.3. Reliability of the set-up

Tests have been carried out to check the reliability of the system. A "loss" in the system could not be resolved and may be due to a "sink" in the measuring device or small leakages in the system. Mathematical analysis of measurements of an "empty run" of 5 days demonstrated a loss proportional to [CO_2].

To account for the "loss," it appeared to be more accurate, however, to rely on the postcarbonation trend of [CO_2] loss (slope S_2 in Fig. 3) to calculate the net CO_2 uptake of the experiments. Experiments with different samples of similar experiments gave acceptable coefficient of variation of 10–20%.

2.4. Data deduced from each experiment

Raw data from the carbon dioxide concentration measuring device are combined in a spreadsheet and represented graphically as in Fig. 3.

The data of the IR device have been combined with the data on temperature and RH. The temperature data were only used to check for an isothermal testing condition. RH measurements aimed at controlling the proper working conditions of the IR device but revealed also an increase of humidity when the carbonation started.

The best way to identify the background loss—over the length of the experiment it can be considered a linear function—is to use the slope S_2 after t_3. On the graph, the validity can be checked as the reference line representing the background loss is calculated backwards starting at the end of the experiment ($t >> t_3$) using S_2. In this way, possible misinterpretation of the time t_3—that would result in a difference between the reference line and the measured value after t_3—can easily be seen (Fig. 4).

In Fig. 5, the net uptake due to carbonation is given. The area between the curve and the *x*-axis represents the amount of carbon dioxide consumed by the carbonation.

The derivative (uptake speed) has been defined revealing the change of speed over the experiment. The max and average speed of carbon dioxide uptake are calculated from the worked data. Graphical representation eased the interpretation. From the graph and the data it refers to, the moment (t_2) and the values of net max uptake have been defined (see Fig. 6).

From the analysis of the data, a number of parameters can be deduced and are summarized for each experiment.

Conversion is done from [CO_2] in % to mmol/m^3 and consequently carbonation speed to mmol/s taking into account the volume of the set-up.

The reliability of the outcome of the experiments (CO_2 uptake speed) has been checked looking at the coefficient of variation of the data for comparable experiments (same lime type, same start [CO_2]), averages have been calculated based on at least 3 reliable data. Data too much out of range have been disregarded and tests were redone as to have at least three valuable tests.

Statistical studies on the data have been used to check for global trends. Data have been normalized to mass units of lime (converted from grams to millimole). As every millimole of CO_2 converts 1 mmol during carbonation, speed values are given in 1/s. A database for analysis, modeling, and study with the following parameters was made.

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1. **ID identification of experiment;**
2. Test type (code);
3. Lime type (code);
4. Level of the [CO_2] (code);
5. **BET area (m^2/g);**
6. **Mean value of particle diameter size (μm);**
7. Net lime mass (mmol);
8. Start [CO_2] (mol/m^3);
9. S_1 (slope before increased CO_2 uptake) (1/s);
10. t_0 (start real uptake) (s);
11. t_1 (moment start of increased CO_2 uptake) (s);
12. t_2 (moment of max uptake speed S_{max}) (s);
13. S_{max} (max CO_2 uptake rate) (1/s);
14. S_{avg} (average CO_2 uptake rate between t_1 and t_3) (1/s);
15. t_3 (moment end of increased CO_2 uptake) (s);
16. S_2 (slope after increased CO_2 uptake) (1/s);
17. D[CO_2] (CO_2 uptake between t_1 and t_3) (mmol);
18. S_{net} (max net CO_2 uptake rate) (mmol [CO_2]/s);
19. $S_{netmax\ calc}$ (max net CO_2 uptake rate) (1/s);
20. $S_{avgnetcalc}$ (calculated average net CO_2 uptake rate) (1/s);
21. Net D [CO_2] (net uptake over whole experiment) (mmol);
22. Net D ($t_3 - t_1$) (net uptake between t_1 and t_3) (mmol);
23. Carbonated part of the lime sample as estimated from the experiment (CarbCalc %);
24. Carbonated part of the lime sample as identified using TA (CarbTA %);
25. **Percentage of $Ca(OH)_2$ in total sample mass at start.**

(bold are material characteristics)

Those results have been used to carry out factor analysis and correlation analysis. Also mean values and standard deviations have been calculated so that confidence intervals could be defined.

2.5. Set-up validation

Fig. 7 shows the maximum uptake speed of tests with different combinations of [CO_2], lime types, and lime masses.

A variety of maximum carbon dioxide uptake rates (absolute values) have been measured between 3.99×10^{-4} and 2.84×10^{-3} 1/s. Results thus refer to the properties of the materials rather than to the property or limits of the set-up.

TA of the uncarbonated and carbonated samples was carried out to determine the amount of water in the sample.

TA in N_2 flushed environment on approximately 20 mg of the carbonated samples has been carried out to check the uptake of carbon dioxide through carbonation. Fig. 8 shows

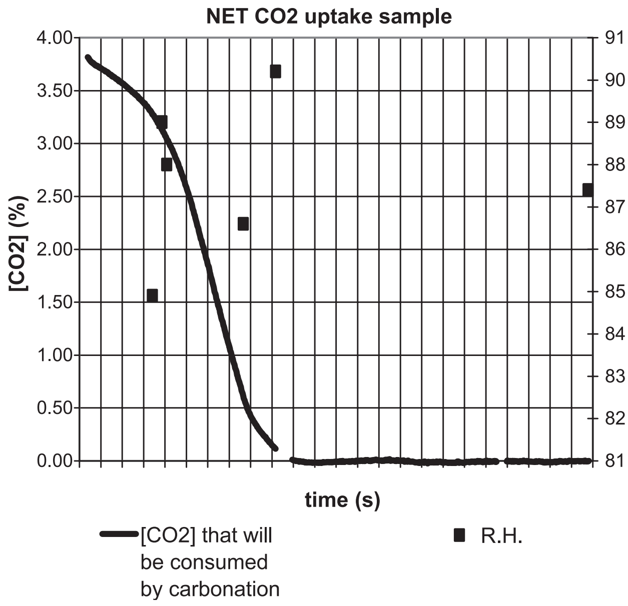

Fig. 5. Net uptake of carbon dioxide due to carbonation.

the relation between the carbonation conversion fraction defined by TA and the calculated one. Difference between both can be due to the difficulty in defining the exact time of the start (t_1) and the end (t_3) of the carbonation, or a difference between the real and defined background carbon dioxide loss defined by the slope S_2. A last factor influencing this difference maybe due to the representativity of the sample as the sample for the TA was approximately 1/20th of the carbonated sample after the carbonation experiment. Nevertheless, the calculated carbonation rate (“Carbcalc”) is a fair approximation of the carbonation rate compared to earlier results. The TA data are the only hard evidence that the uptake of carbon dioxide is due to the carbonation reaction.

Spreading of the different uptakes measured and control using TA prove the validity of the set-up.

It is interesting to notice that with the set-up a high degree of carbonation can be reached. This differs from the carbonation conversion fraction reached in set-up at temperatures between 60 and 90 °C as described in Ref. [5] where up to 35% of conversion has been reached between 10 and 20 min.

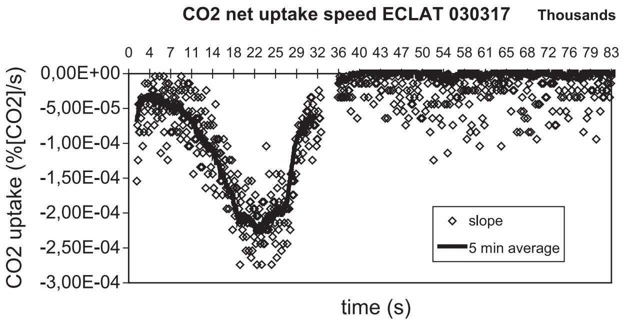

Fig. 6. Net uptake speed due to carbonation.

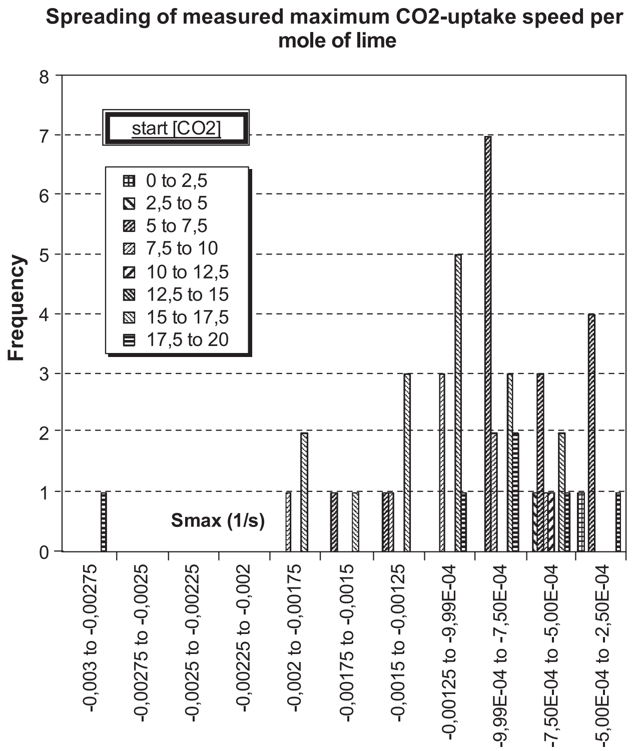

Fig. 7. Histogram of measured maximum uptake rates (S_{max}) (1/s) for various start CO_2 concentrations (mol/m^3) at start.

TA results show that no full carbonation is reached. This is due to the creation of an “impermeable” layer of calcium carbonate around the lime hindering further penetration of carbon dioxide to the uncarbonated core. Parallel to these experiments, carbonation has been

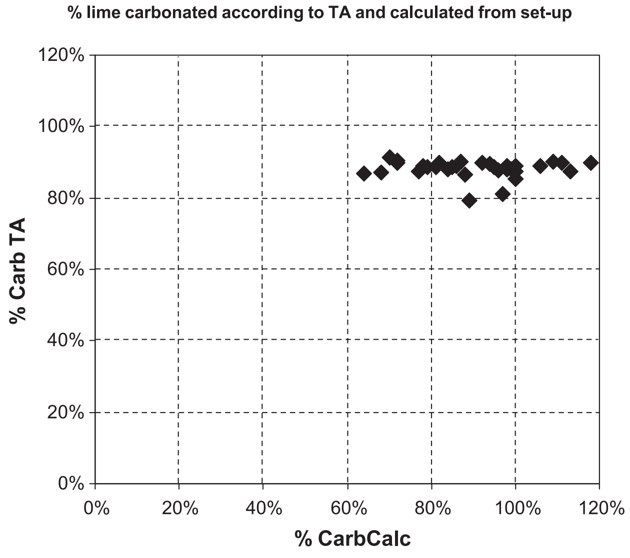

Fig. 8. Comparison of carbonation rate defined from TA (CarbTA %) compared to calculated amount of carbonation defined through carbon dioxide data (CarbCalc %) (TA carried out by J. Druzik at GCI).

studied under optical microscopy. Large-scale portlandite crystals have been carbonated and the formation of such impermeable layer was seen. This phenomenon is similar as the one addressed by Sohn and Szekeley [29] for porous solid pellets, where intragrain diffusion resistance may become so large that it will control the progress of the reaction process.

A single ongoing carbonation process thus seems to end before all portlandite is carbonated. This conclusion is not without interest for understanding some traditional building practices using lime. It is an ancient practice to wet and dry lime mortar to improve its carbonation. The abovementioned microscopy study also revealed that wetting and drying in an early phase leads to the detachment of the outer layer of carbonated material from the inner uncarbonated one. This can be explained by the fact that portlandite is more soluble than the calcite layer so that when water reaches the interface, detachment can occur. When no carbon dioxide “impermeable” layer could be formed, the possibility to reach full carbonation is thus improved.

3. Results

3.1. Parameters of the experimental conditions

Different lime samples have been carbonated using the set-up at starting carbon dioxide concentrations of approximately 7 and 17 mol/m^3. Most samples contained approximately 2.5 mmol of $Ca(OH)_2$. For ECL lime, only a limited number of additional tests have been carried out at intermediate carbon dioxide concentrations (10, 4, and 2 mol/m^3) and more variation of lime sample mass.

3.2. Sample preparation and material properties

Samples consisted of lime putty smeared on a plastic cup for easily removal from the sample holder and control of weight change. Putties were prepared from different types of lime hydrate and one lime putty.

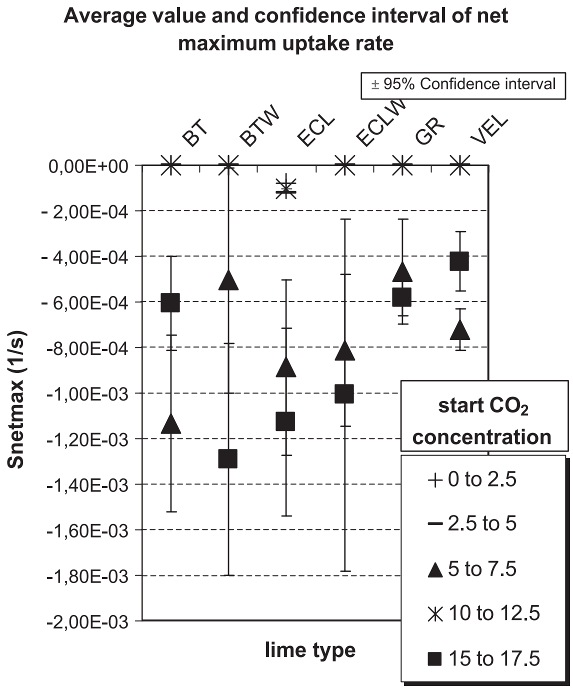

Fig. 9. Average value and confidence interval of net maximum uptake rate due to carbonation related to different levels of carbon dioxide concentration (mol/m^3).

Table 1
Physical properties of tested lime, weight fraction of lime available for carbonation

		BET (m^2/g)	PSD, mean value (μm)	Percent lime in sample
GR	Putty	11.60	5.01	50
VEL	Dry hydrate	14.14	4.68	84.2
	Putty	22.20	2.97	64
ECL	Dry hydrate	17.89	4.68	88.4
	Putty	29.02	3.15	55
	Putty extra water (ECLW)	31.86	3.30	44
BT	Dry hydrate	43.73	5.37	90.4
	Putty	43.50	2.89	57
	Putty extra water (BTW)	44.30	3.47	44

BET is defined on dried materials, PSD was measured in ethanol.

- Laboratory grade dry calcium hydrate (VEL)
- Commercial dry calcium hydrate (ECL)
- Experimental lime type with a higher specific surface and similar particle size distribution as ECL (BT)
- Lime putty slaked for a very long time, received from Greece (GR)

Mixing those materials with water and storing them for some time before sampling resulted in testing samples with different grain structure and specific surface. The particle size distribution (PSD) has been measured using a Shimadzu Sald 3001 Laser Diffraction Particle Size Analyzer, the samples were dissolved in ethanol. The BET values are N_2 surface area measurements carried out in a Micrometics-Gemini 2360.

A summary of the lime properties is given in Table 1.

Some comments can be made regarding the material structure modification when wetting dry lime hydrate: The specific surface of VEL and ECL increases when hydrate is turned into putty, this is not the case for BT. ECL and BT have rather similar PSD; nevertheless, there is a considerable difference in specific surface (BET). The PSD changes towards lower mean values when putty is made of BT; however, the specific surface does not change in that case. It seems to indicate that BT lime hydrate consist of a porous conglomerate of lime particles that adhere enough to be measured as single particles when PSD is measured.

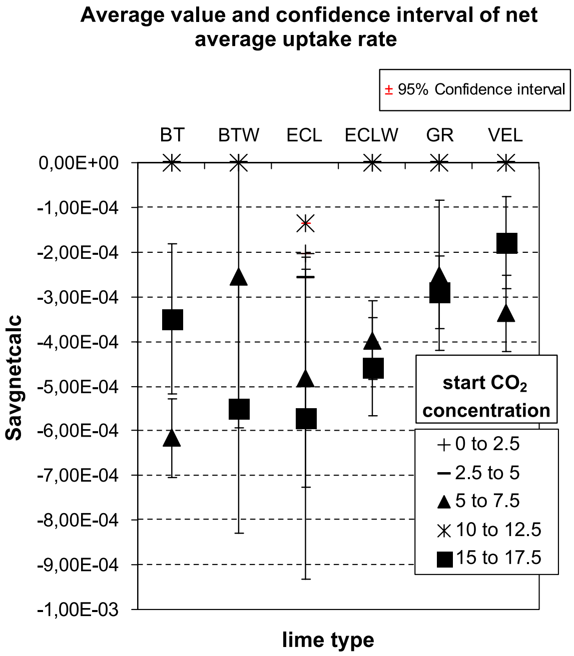

Fig. 10. Average value and confidence interval of net average uptake rate due to carbonation related to different levels of carbon dioxide concentration (mol/m^3).

As each lime sample contained some water and part of the initial lime hydrate was carbonated, the net available portlandite of each sample was defined as a fraction of the sample weight. Those values have been defined using TA on the initial material and on samples before carbonation.

3.3. Results summary

An overview of 49 uptake rates measured in the experimental set-up—represented as negative values as the concentration is dropping—is given in Figs. 9 and 10. The average net CO_2 uptake speed (1/s) and maximum net CO_2 uptake (1/s) are presented. They correspond with the measured average and maximum uptake of carbon dioxide minus the background loss (S_2) within the boundaries t_1 and t_3. Values are grouped according to the lime type and the level of carbon dioxide concentration at the start of the experiment. The mean value and the 95% confidence interval for each lime type and start concentration are given.

4. Discussion

From the results database, a correlation study has been carried out. From factor analysis on all data for all different lime types and testing conditions, the following factors are identified:

Factor 1 is related with the set-up conditions: [CO_2], S_1 and S_2;

Factor 2 is related with the speed measurements (S) and the carbonation process: mass, t_1, duration;

Factor 3 is related with the material properties: BET and mean particle size.

Factor 4 is related with the degree of carbonation reached: net uptake and % carbonated;

Some of the factors are obvious. The aim of the research is to define which material property influences carbonation rate and to check the relation between carbonation rate and carbon dioxide concentration.

4.1. Set-up conditions

The slopes S_1 defining the initial uptake of carbon dioxide before carbonation has started and the background loss (S_2) are linearly and proportionally dependent on the carbon dioxide concentration in the set-up. For S_1, the R^2 value is .45 and for S_2 the R^2 value is .76. Regarding S_2, it can be explained as the amount of CO_2 needed to equilibrate the gas and the water is greater when the concentration is higher. It is easily understood that also the background loss, depending on a variety of features of the set-up such as uptake, is proportional to the concentration.

4.2. Reaction rate and interdependency

The different types of uptake rate defined, including the net uptake rates, vary with the progress of time. As speed data are unified to mass, it is logical that when the speed increases the duration of the carbonation decreases.

More surprising is the fact that there is a correlation between the net uptake speed and the mass (Fig. 11)—although uptake rates have been unified to mass. This points into the direction that still some diffusion might affect the uptake rate.

There is no correlation between uptake speed and initial carbon dioxide concentration in the gas (Fig. 12). Carbonation reaction, contradictory to the earlier mentioned assumption in [1], seems to be independent from the carbon

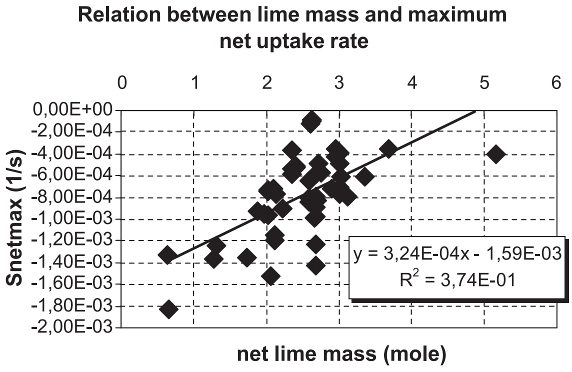

Fig. 11. Relation between maximum uptake rate (calibrated to mass) and sample mass.

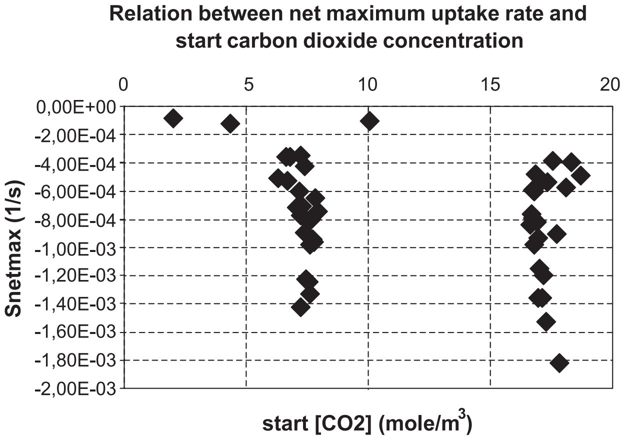

Fig. 12. Relation between maximum uptake rate and start carbon dioxide concentration.

dioxide concentration in the ambient air for the conditions studied here. This indicates that the controlling factor in the carbonation reaction is the dissolution of portlandite in the aqueous medium in which the reaction occurs. The transfer of carbon dioxide from the gas in the water is so fast that for the level of CO_2 concentrations studied (7–17% vol.% CO_2), this is no controlling factor. Shin-Min Shih et al. [5] report on carbonation tests carried out at temperatures between 60 and 90 °C and at CO_2 concentration between 3.15 and 12.6 vol.%. Similarly to the results presented here, they concluded that the carbonation reaction is zeroth order with respect to CO_2 concentration range of their study.

4.3. Reaction rate and lime properties

This study wants to identify whether there is a relation between carbonation speed and material properties. The net maximum and average uptake rate best correlate with the specific surface of the lime (Fig. 13) rather than with the mean particle size (Fig. 14). The highest measured uptake rate (the most negative value) of each lime type clearly increases with increasing BET value of the lime.

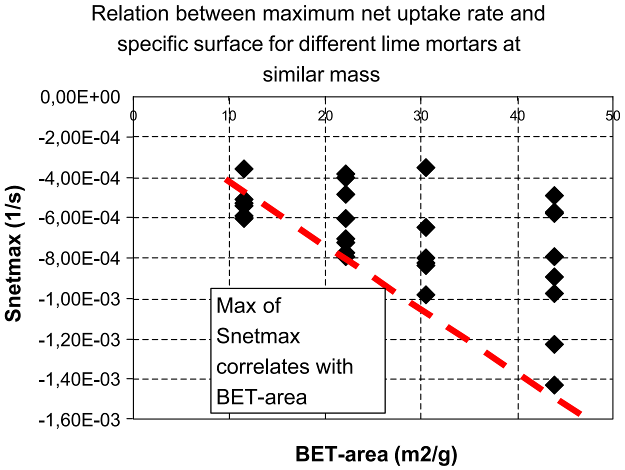

Fig. 13. Realtionship between specific suraface of lime and net maximum uptake rate.

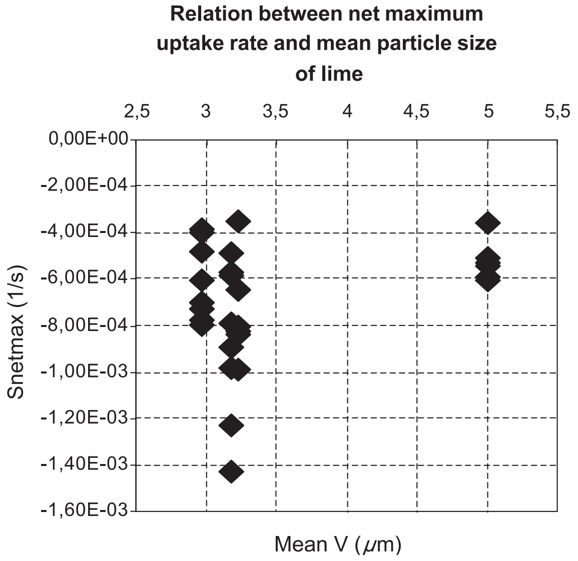

Fig. 14. Relationship between net maximum uptake rate and mean particle size of lime.

5. Conclusions

An experimental set-up has been designed and validated that allow measuring the speed of the carbonation reaction between lime and carbon dioxide at 20 °C. TA has been used to check the carbonation process and to identify the properties of the raw materials and samples.

In the experimental set-up, the reaction rate is defined by measuring reduction of carbon dioxide concentration in a closed system. This procedure avoids possible errors that might occur when using weight gain as a possible measure for carbonation progress due to the interference that might result from weight gain resulting from water produced during carbonation.

Limes with different physical properties have been subjected to carbonation experiments at various carbon dioxide concentrations. Data collected from the various tests allow identifying the conditions and material properties influencing the carbonation process.

Data show that unlike stated in a previous publication on modeling lime mortar carbonation but in agreement with recent publication on carbonation of lime at temperatures between 60 and 90 °C, the carbonation reaction is zeroth order with respect to carbon dioxide concentration in the range (15–50%) of this study at ambient temperature (20 °C). The controlling factor in the carbonation process may be the dissolution of lime at the water-adsorbed surface. Due to the difference in reaction conditions—there is much more water present to dissolve lime in the case of water treatment applications—the latter models should be used with caution when studying carbonation of lime mortars. The highest reaction rate is proportional to the specific surface of the lime when other factors are kept constant.

From the TA on the carbonated samples, an interesting finding has been made that is of use in understanding some traditional building practices using lime. It has been noticed that a single ongoing carbonation process ends before all lime is carbonated. It is an ancient practice to wet and dry lime mortar to improve carbonation. The explanation given for this improvement assumes that it is due to the detachment of the outer carbonated layer from the inner uncarbonated one, as portlandite is more soluble than the calcite layer.

Nomenclature

D_{effc}: effective carbon dioxide diffusion coefficient (m^2/s)
$R(w,c)$: reaction speed per unit of lime mortar [mol/(s m^3)]
w: water content (kg/m^3)
$[CO_2]$: carbon dioxide concentration in the air of the pore in (mass%) or (mol/m3);
$\beta([Ca(OH)_2])$: ratio of pore surface taken in by lime over the total pore surface
$Ca(OH)_2$: amount if lime present in mortar at certain time;
$[Ca(OH)_2]_O$: amount if lime present in mortar before carbonation;
α(RH): influence of RH on reaction term;
Ψ: porosity of lime mortar

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