Influence of Climatic Conditions on the Carbonation of Quicklime

R.-M. Dheilly, J. Tudo, and *M. Quéneudec*

The influence of relative air moisture, temperature, and concentration of CO_2 on the carbonation of CaO have been studied in normal climatic conditions. The CaO used for this original work is a granular material prepared by calcination of pure $CaCO_3$. The influence of time and mechanical treatment has been studied, too, to obtain a complete carbonation. A model of hydration and carbonation has been established to explain the observed phenomena.

This work was carried out with the view to defining the optimum conditions for the storage of quicklime. The results show that the risk of carbonation of quicklime are low in usual manufacturing industry conditions.

1. Introduction

There have been a great number of publications on the subject of the carbonation of quicklime. As a general rule, however, they are based on the use of high-temperature and high-pressure conditions. For example, Glasson examined the action of CO_2 on CaO at 1023 K using a pressure above 1 atm and at 773 K for 0.5 atm pressure below 1 atm (Ref 1). In experiments on the action of CO_2 on CaO carried out between 1962 and 1989 (Ref 2 to 7), the main purpose was to define the kinetics of recarbonation of CaO in temperatures between 673 and 1123 K. Oakeson and Cutler (Ref 8), in their studies on the reversibility and transformation of $CaCO_3 \leftrightarrow CaO$, showed the effects of CO_2 pressure that varied between 2.53 and 24.67 atm, at temperatures between 1126 and 1317 K.

These conditions, however, do not correspond to the way lime is used when applied to the construction industry. To keep within the fields compatible with normal climatic conditions, this study looks at the influence of relative air moisture, temperature, and the concentration of CO_2 on the way granular materials behave.

2. Material and Experimental Procedure

2.1 Raw Material

The CaO used in the study was in powder form. It was synthesized in order to guarantee maximum purity and to avoid interference from any secondary products.

Pure $CaCO_3$ was heated to 1173 K in a gas-filled atmosphere with no CO_2 present (oxygen was used). The rise in tempera-

R.-M. Dheilly, J. Tudo, and **M. Queneudec,** Equipe Conception et Evaluation des Procédés et Systèmes de la Construction, Laboratoire Matériaux, Structure, Thermique, Université de Picardie—Institut Universitaire de Technologie, Avenue des Facultés, 80025 Amiens Cedex 1, France.

ture took place over one hour and was maintained for 15 minutes. The CaO was then cooled in the presence of oxygen.

The temperature of 1173 K was determined following the results of previous studies concerning the influence of temperature during the calcination of $CaCO_3$ in the production of CaO (Ref 9). The studies show that the reaction of a substance produced from decomposition is linked to (1) the maximum temperature at which separation occurs; and (2) the time during which maximum temperature must be maintained, giving rise to the growth of granules, which influences the texture data (specific surface and volume of porosity), and in turn determines the reactivity.

At 1273 K, no $CaCO_3$ was present and the CaO was no longer reactive. At low temperatures (973 K), some $CaCO_3$ was always present and the CaO was reactive. The temperature of 1173 K was chosen as a result of numerous experiments made at temperatures between 973 and 1273 K. In each case, the purity of the oxide was checked by x-ray analysis using the diffraction technique and thermogravimetric analysis.

From the image produced by a scanning electron microscope (Fig. 1), the CaO obtained by the above-mentioned method is in a granular form of less than 10^3 nm. The extremely porous nature of each granule is spread homogeneously throughout. The porosity is due to the evacuation of CO_2. This corresponds to a product that would be known in industrial terms as "highly reactive." The specific surface being equal to 5.1 m^2/g and the cumulative adsorption pore area plot (Fig. 2) are confirmation of the reactivity. The greater part of the specific surface corresponds to below 10 nm pore diameter.

2.2 Experimental Techniques

The characterization of the prepared CaO was measured by the use of:

- MEB PHILIPS SEM 505 electron microscope (Université de Picardie Jules Verne, Amiens, France) for microscopic observations
- Laser diffraction on CILAS Type HR 850 (Cilas, France) to determine granule size

- Micrometrics ASAP 2000 ET (Unité de Recherche Nivelles, Nivelles, Belgium) to determine specific surface analysis and volume of porosity

The climatic studies were done using the installation shown in Fig. 3. The first temperature-controlled chamber (1) main-
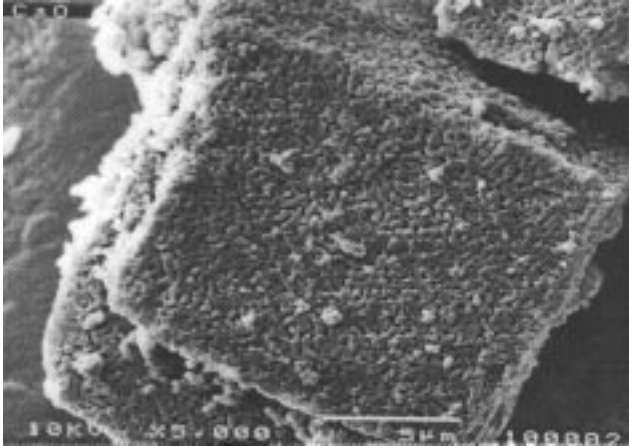

Fig. 1 Scanning electron micrograph of the CaO prepared by calcination of CaCO$_3$, at 1173 K in a gas-filled atmosphere with no CO$_2$ present. (Art has been reduced by 70 percent for printing.)
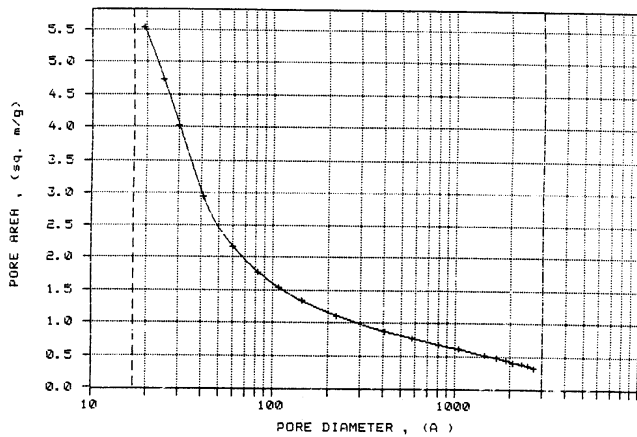

Fig. 2 Cumulative adsorption pore area plot (B.E.T. method)
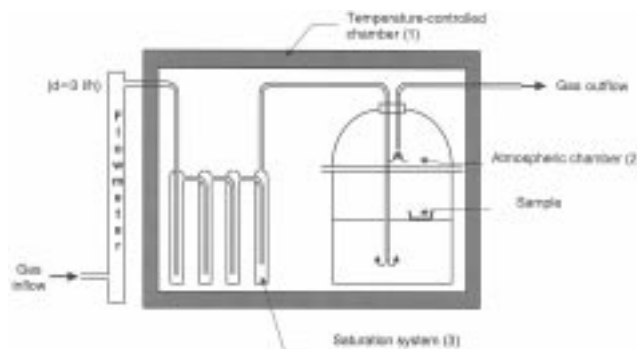

Fig. 3 Experimental apparatus

tained the desired temperature of the entire atmospheric chamber (2) and of the saturation system (3). The atmosphere in the atmospheric chamber was maintained at the desired level through the circulation of gas from the saturation system (3). The relative humidity (RH) of 30 or 60% was obtained through the use of a mixture of water and sulfuric acid (17.82 M), which was constantly renewed. The concentrations were, respectively, 775 and 495 g/L of acid. The experimental apparatus and the insignificant amount of pressure of H$_2$SO$_4$ prevented the formation of calcium sulfate, which was confirmed by subsequent analysis. In each case, the amount of gas introduced into the apparatus was metered in order to ensure that the experimental conditions were constant. The size and shape of the sample dish determined the number of moles of the sample required to obtain a thin layer of powdered material (i.e., 8.93×10^{-3} moles or 504 mg of CaO in terms of the mass).

During the trials each sample was monitored using:

- Gravimetric analysis: weighing every 12 hours
- X-ray diffraction analysis, using a SIEMENS Kristalloflex 700 generator (Université de Picardie, Amiens, France), was carried out every 12 hours on the second sample, which was identical to that used in the gravimetric analysis, and placed in the same conditions.

Because the presence of Ca(OH)$_2$ and CaCO$_3$ in a sample can be obtained by chemical analysis, the level of Ca(OH)$_2$ was found by using the dosage method described in the NBN B 13-2032 Standard, and the percentage of CaCO$_3$ was measured by using the Dietrich-Frühling calcimeter (Université de Picardie, Amiens, France).

A method of dosage by thermogravimetric analysis was developed by the authors in order to quickly determine the composition of each of the sample. The tests were carried out using a SETARAM 92 microthermoscale (Université de Picardie, Amiens, France) in dried oxygen conditions with the heating rate set at 40°/h. Loss of matter occurs between 648 and 693 K for the hydrating water, and between 913 and 1083 K for the decarbonation. The loss of matter at lower temperatures shows that the samples contained "free" water, or water only weakly linked.

3. Experimental Results and Analyses

Figures 4 and 5 show the influence of temperature and hygrometry on samples subjected to extreme concentrations of CO$_2$. The minimum level corresponds to air which has low levels of pollution (i.e., 0.03% of CO$_2$). The maximum level was at one carbonic atmosphere. The temperatures chosen are those found in temperate climatic conditions. An average RH of 60% is found in this type of climate. Humidity levels of 30 and 100% are extreme conditions that can be compared with storage conditions in a silo and during periods of high humidity. These diagrams show that the theoretical mass of the sample has been completely transformed into Ca(OH)$_2$ and CaCO$_3$.

a : relative humidity : 30 %
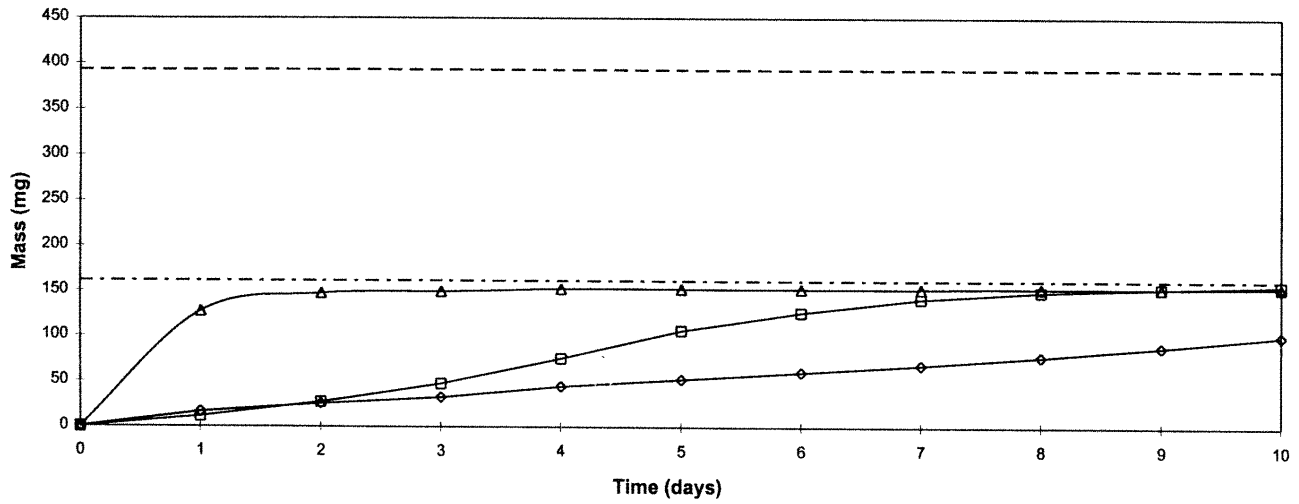
b : relative humidity 60 %

c : relative humidity 100 %

Legend:
— ◇ — T=10°C   — ☐ — T=20°C
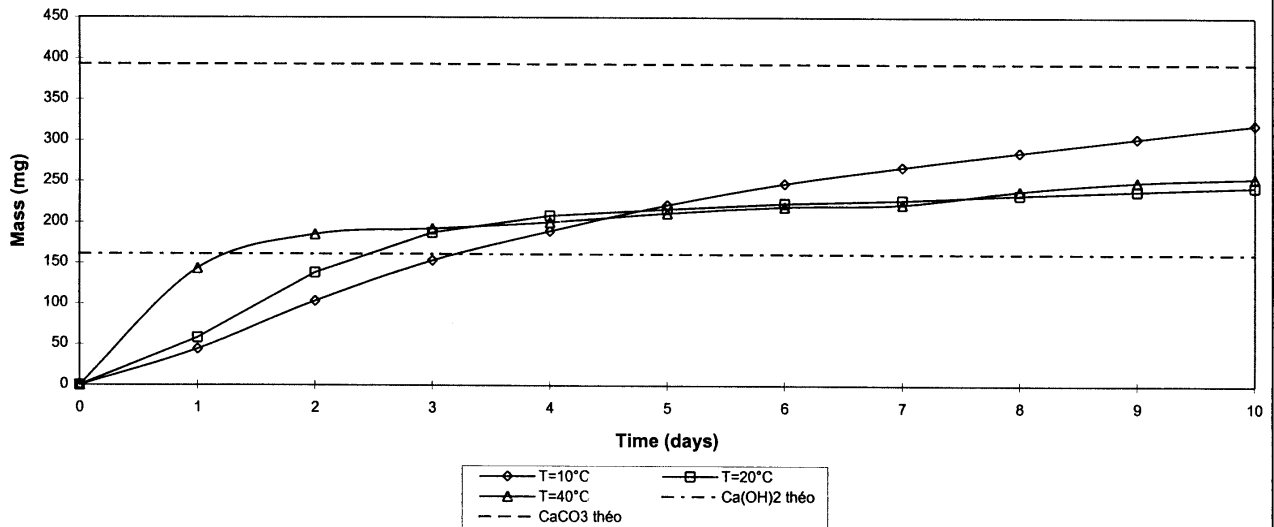— △ — T=40°C   — · — · — Ca(OH)2 théo
— — — CaCO3 théo
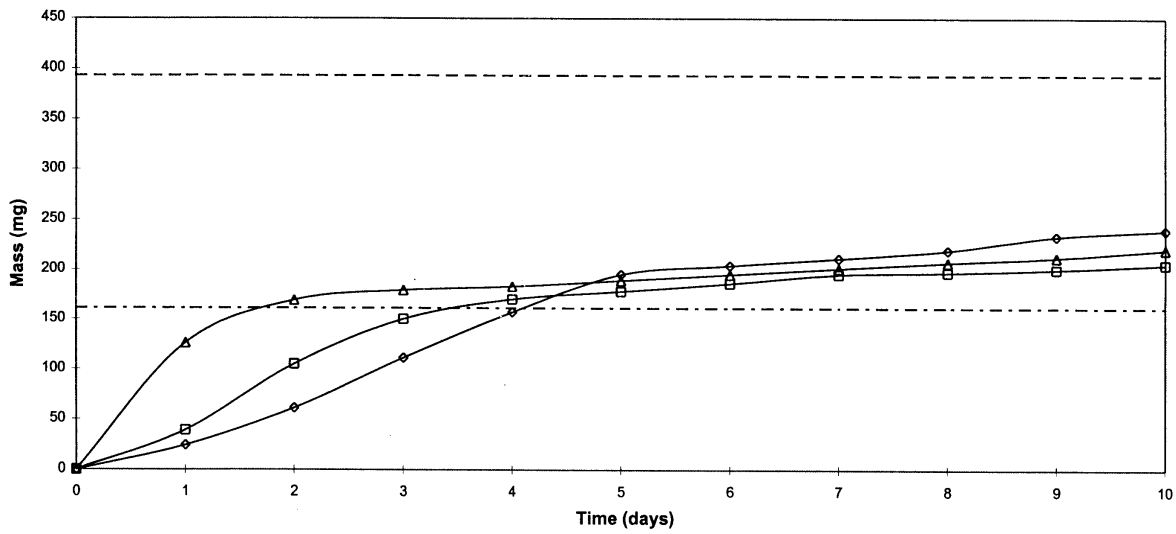
Fig. 4   CaO in an atmosphere poor in CO_2. (a) 30% RH. (b) 60% RH. (c) 100% RH
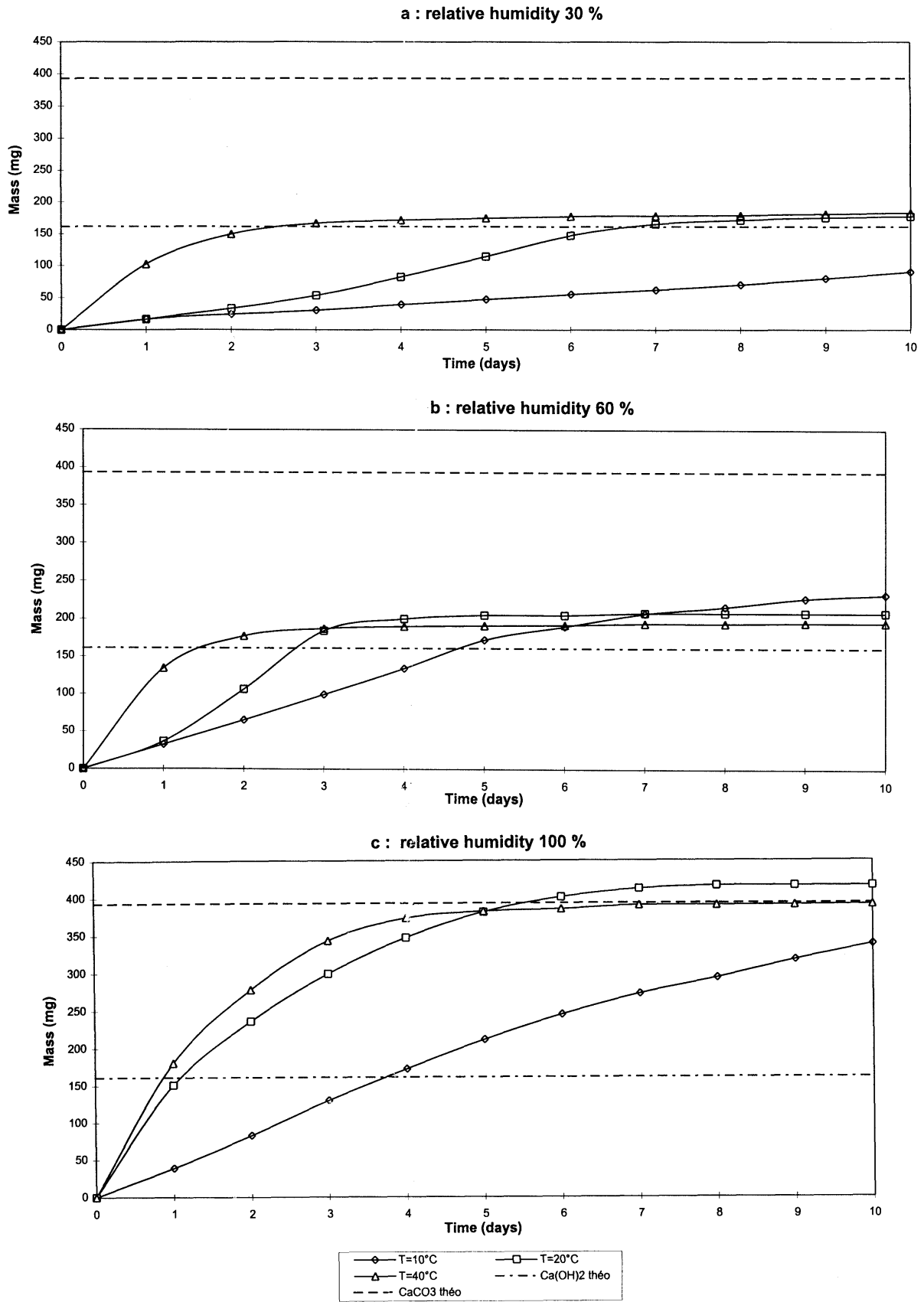
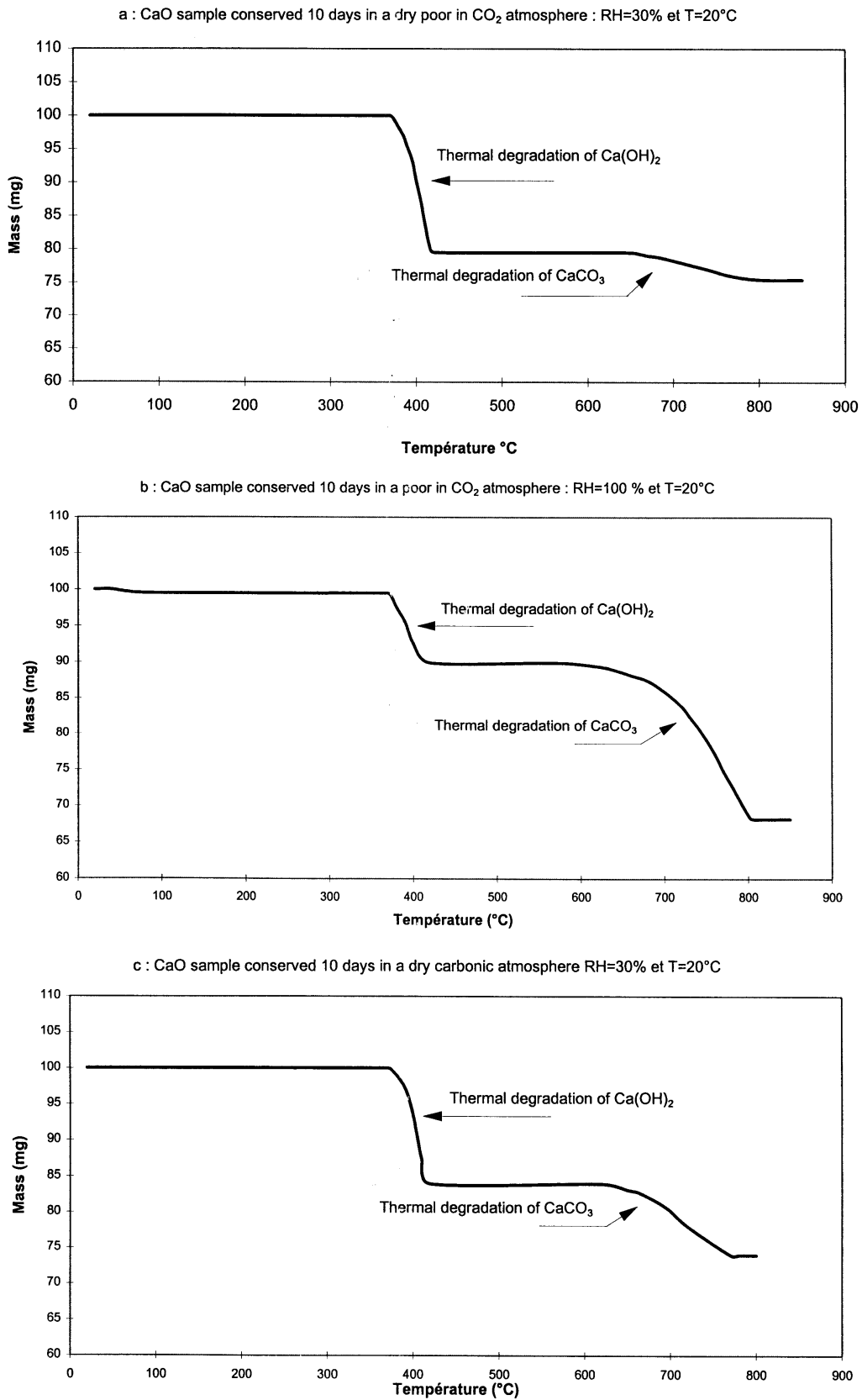**Fig. 5** CaO in a carbonic atmosphere. (a) 30% RH. (b) 60% RH. (c) 100% RH

Fig. 6 Thermogravimetric analysis (dry O_2, speed: 40°/h). (a) CaO conserved 10 days in a dry atmosphere with a low level of CO_2, RH = 30% and T = 20 °C. (b) CaO conserved 10 days in a "wet" atmosphere with a low level of CO_2, RH = 100% and T = 20 °C. (c) CaO conserved 10 days in a dry carbonic atmosphere, RH = 30% and T = 20 °C

3.1 Atmospheric Influence

In an Atmosphere Poor in CO_2. Figure 4(a) shows the evolution in a dry atmosphere (RH = 30%) with a low level of CO_2. At 40 °C, stabilization of the mass has been reached at the third day. At 20 °C, it needs 10 days, and at 10 °C, it is very slow.

At an RH level of 60% (Fig. 4b), the evolution toward the stabilization of the mass occurs in the same way. The higher the temperature, the faster stabilization is attained. However, from the fifth to the sixth day, the increases in mass are greater for a temperature of 10 °C. The reaction is the same but increases when RH reaches 100% (Fig. 4c). The different elements present after 10 days in an atmosphere low in CO_2 were determined by thermogravity. An analysis of the results showed the following:

- In the case of low relative humidity (RH = 30%), the mass of the sample never goes above that which it would have had if it had been completely changed into hydroxide. The three elements CaO, $Ca(OH)_2$, $CaCO_3$ were present. At 20 °C, the distribution is as follows: 7% $CaCO_3$, 85.3% $Ca(OH)_2$, and 7.7% CaO unchanged (Fig. 6a). The percentage of carbonation is low in these conditions of relative humidity. It increases as the temperature rises: 17.6% at 40 °C.
- When the ambient humidity rises, the proportion of carbonate obtained after 10 days rises: 18% at 60% RH and 40.7% at 100% RH, at a constant temperature of 20 °C (Fig. 6b).
- Thermogravimetric tracking and analysis by x-ray diffraction show that for RH equal to or above 60%, temperature plays an important role in the carbonation of the hydroxide. Note that the three types resulting from the reaction show that the two transformations (1) CaO → $Ca(OH)_2$ and (2) $Ca(OH)_2$ → $CaCO_3$ overlap one another. The transformation (2) was faster at 10 °C than at any other temperature.

In a CO_2 Atmosphere. The analysis of the results obtained in an atmosphere of CO_2 lead to the following conclusions:

- The quantity of CO_2 in the chamber does not change the speed of the transformation from oxide to hydroxide, regardless of temperature variations or whether the RH is 30 or 60%. The transformation of (1) CaO → $Ca(OH)_2$ evolves with the change in temperature.
- The concentration of CO_2 has an influence on the hydroxide carbonation. As shown in Fig. 5(a), at RH = 30% and after 10 days, a percentage (in terms of mass) of 18.31% of $CaCO_3$ was obtained, compared to 7% of $CaCO_3$ in an air-filled atmosphere at 20 °C (Fig. 6c).
- When the ambient humidity is low (RH = 30%), whether at 40 °C or at 20 °C after the transformation (1) CaO → $Ca(OH)_2$, the hydroxide evolves very slowly and the carbonation remains weak. It increases as RH increases. At RH = 60%, the quantity of carbonate obtained increases in direct relation to the reduction in temperature (34.6, 36.9, and 40.2% for the 40, 20, and 10 °C temperatures, respectively). However, at RH = 100%, the carbonation increases in direct relation to the rise in temperature. Figure 5(c) shows that at a temperature of 20 °C, the sample mass exceeds the limits of the mass of the completely carbonated CaO. This can be explained by the fact that water has been retained in the sample. As opposed to the previous observation for all the samples examined, in the instant case "free" water was liberated toward 30 °C (Fig. 6b).
- As opposed to the observations made in an atmosphere low in CO_2 at 60% RH, the carbonation seemed to come to a halt at 5 and 3 days for temperatures at 20 and 40 °C. A crystallographic analysis shows the presence of CaO, $Ca(OH)_2$, and $CaCO_3$. At 100% RH, however, even if the existence of the two steps (1) CaO → $Ca(OH)_2$ and (2) $Ca(OH)_2$ → $CaCO_3$ has been confirmed by X-Ray analysis, the thermogravimetric analysis of a 10-day cured sample does not give proof of the $Ca(OH)_2$ presence, with the composition of 92.5% $CaCO_3$, 0% $Ca(OH)_2$, and 7.5% CaO (unchanged), at 20 °C. The results were confirmed by chemical analysis of the sample.

Table 1 Sample composition as a function of the exposition time in two different atmospheres (carbonic or with a low level of CO_2): RH = 100% and T = 20 °C.

These percentages have been determined by thermogravimetric analysis

Atmosphere	Composition	10 days	20 days	40 days	60 days	80 days
Atmosphere with a low level of CO_2(0.03%)	%CaO → $CaCO_3$	40.5	85.2	88.35	92.01	92.04
	%CaO → $Ca(OH)_2$	43.8	6.5	3.57	0	0
	% unchanged CaO	15.7	8.3	8.06	7.99	7.96
Carbonic atmosphere	%CaO → $CaCO_3$	92.48	92.51	92.54	92.54	92.56
	%CaO → $Ca(OH)_2$	0	0	0	0	0
	% unchanged CaO	7.52	7.49	7.46	7.46	7.44

Table 2 Sample composition as a function of the mechanical treatment and the exposition time in two different atmospheres (carbonic or with a low level of CO_2): RH = 30% and T = 40 °C.

These percentages have been determined by thermogravimetric analysis

Atmosphere	Composition	10 days without grinding	10 days: grinding every 3 days	30 days without grinding
Carbonic atmosphere	% CaO → $CaCO_3$	17.6	37.7	39.5
	% CaO → $Ca(OH)_2$	65.2	49.9	42.2
	% unchanged CaO	16.5	12.4	14.3
Atmosphere ith a low level of CO_2 (0.03%)	% CaO → $CaCO_3$	6.8	10.7	7.9
	% CaO → $Ca(OH)_2$	74.1	77.4	73.6
	% unchanged CaO	19.1	11.9	18.5

3.2 The Time Influence

The previous results showed that it was impossible to obtain complete transformation of CaO into $CaCO_3$ after 10 days. Studies were carried out over a longer period. The results, given in Table 1, were obtained over 80 days at RH = 100% and $T = 20$ °C.

It can be seen that in a humid carbonic atmosphere, carbonation does not evolve greatly after 10 days. The presence of hydroxide was not detected. In an atmosphere low in CO_2, the same result was obtained but at a later period. It can be deduced that the carbonation stops when the oxide can no longer become hydroxide.

3.3 The Influence of Mechanical Treatment

It appears that the kinetics and the progress in the reaction are linked to the reactivity of the surface. Regular grinding could renew the active areas. The results obtained from grinding the sample and those obtained when the sample is not ground, at RH = 30% and $T = 40$ °C, are presented in Table 2. It shows that grinding improves carbonation in a carbonic atmosphere. In conditions low in CO_2, the phenomenon can be observed but is less evident even if the hydroxide transformation is high. This is likely due to the level of ambient CO_2.

4. Synthesis and Conclusions

The results of the experiments show two distinct phases, (1) $CaO \rightarrow Ca(OH)_2$ and (2) $Ca(OH)_2 \rightarrow CaCO_3$, that can be explained as:

1. In a humid atmosphere, the nucleii in the grains of CaO, through the action of H_2O, are attacked, bringing about the formation of $Ca(OH)_2$ on the outer surface of the grains. The most likely mechanism for this would be as follows, according to Langelin (Ref 10):

$$Ca\!-\!O + H^+\!-\!OH^-$$

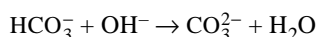$$CaOH^+ + OH^- \rightarrow Ca(OH)_2$$
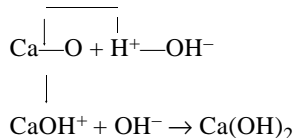
2. The hydroxide formed by this method absorbs water in direct proportion to the relative humidity and the temperature. It is partly dissolved into $Ca^{2+} + 2\,OH^-$. At the same time, the ambient CO_2, in which the solubility varies with the temperature (Ref 11), dissolves to form ions of CO_3^{2-} where the pH is high.
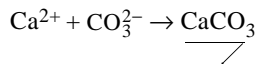
- Solubilization of $Ca(OH)_2$:

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2\,OH^- \;(pH > 10)$$
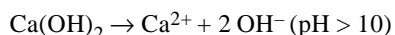
- Diffusion and dissolving of CO_2:

$$CO_2 + OH^- \rightarrow HCO_3^-$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

- Overlaying of the reactions going from solid to liquid to gas:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \nearrow$$

Each grain is covered by a layer of $CaCO_3$. Carbonate formed by this method has a low porosity and, as a result, isolates the remaining oxide and hydroxide, thus slowing down the reaction. Over the period these experiments were carried out, a complete reaction was never obtained. This explains why $Ca(OH)_2$ is formed in normal atmospheric conditions when the humidity was low, but it practically never progresses toward becoming $CaCO_3$. It also explains why the carbonation of $Ca(OH)_2$ is faster at 10 °C than at 40 °C. At 10 °C, CO_2 dissolves (and diffuses) in higher proportions. This phenomenon constitutes the phase that restricts kinetics.

Moreover, this observation is of greater value in normal atmospheric conditions than in a CO_2 atmosphere where the dissolved CO_2 is always sufficient, irrespective of temperature. During the first phase, the hydration of CaO imposes its own kinetics. $CaCO_3$ is more quickly obtained at 40 °C than at 10 °C.

The work was carried out with the view to defining the optimum conditions for the storage of CaO. The process is usually carried out in storage silos at relative humidities approaching 30% and temperatures not rising above 40 °C within the mass, where atmospheric conditions are assumed to be low in CO_2. The time period involved is no longer than 10 days. The results of this study show that the risk of carbonation is low. The conditions usually adhered to in the manufacturing industry guarantee the high quality of the goods being delivered.

Acknowledgments

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