



## In situ kinetic measurements of gas–solid carbonation of $\text{Ca}(\text{OH})_2$ by using an infrared microscope coupled to a reaction cell

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### ARTICLE INFO

#### Article history:

Received 4 February 2010

Received in revised form 21 April 2010

Accepted 21 April 2010

#### Keywords:

Calcium carbonate

Adsorbed water

Gas–solid carbonation

Calcium hydroxide

Infrared microscope

$\text{CO}_2$  mineralization

### ABSTRACT

Gas–solid carbonation experiments were carried out by using an infrared microscope coupled to a reaction cell. The hydroxide ions ( $\text{OH}^-$ ) consumption and the production of molecular water ( $\text{H}_2\text{O}$ ) and carbonate ( $\text{CO}_3^{2-}$ ) vibration bands were directly monitored as a function of time. Herein, we demonstrated that the gas–solid carbonation of calcium hydroxide (or portlandite) was exclusively activated by initial adsorbed water–molecules (water activity  $\approx 0.6$  in the lab room) at low temperature ( $30^\circ\text{C}$ ) and low  $\text{CO}_2$  pressure (0.5–1.5 bar). We assume that carbonation reaction was then rapidly autocatalysed by the water production and followed by a passivation step due to the formation of a dense layer of carbonate around the reacting particles of portlandite. The fast carbonation and passivation steps were satisfactorily fitted by using a kinetic pseudo-second-order model. Moreover, the infrared measurements provided complementary insights with relevance to the reaction mechanism of gas–solid carbonation of calcium hydroxide. Herein, the formation of metastable aragonite was identified and a hydrated calcium carbonate was suspected during carbonation process.

On the other hand, when initial adsorbed water onto reacting particles was removed by in situ vacuum drying ( $P < 10^{-5}$  mbar,  $T = 110^\circ\text{C}$ ) prior to injection of  $\text{CO}_2$  in the reaction cell (water activity  $\approx 0$ ), the carbonation of calcium hydroxide particles was no more detected by infrared spectroscopy at low temperature ( $30^\circ\text{C}$ ). However, there was evidence for a very limited carbonation reaction at higher temperature ( $300^\circ\text{C}$ ) and low  $\text{CO}_2$  pressure ( $< 1$  bar). Another carbonation mechanism is required to explain this observation, for example the migration of oxygen atoms from the solid towards adsorbed  $\text{CO}_2$ .

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## 1. Introduction

### 1.1. General comments

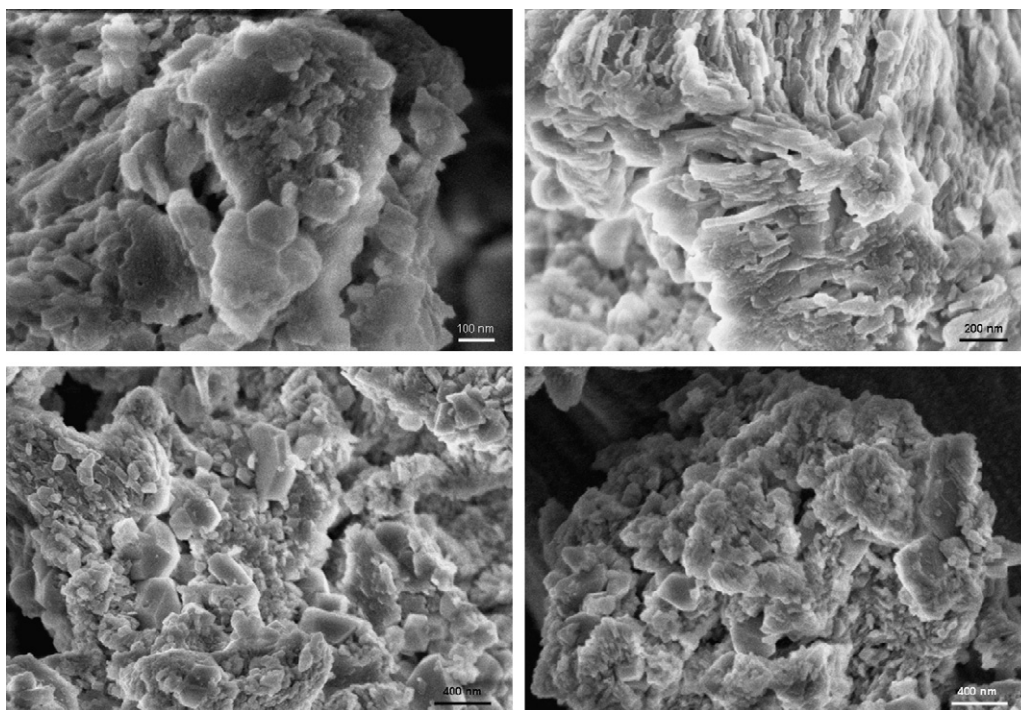
In the last three decades, considerable progress has been observed on the experimental and numerical simulations of physicochemical reactions at the solid–fluid interfaces. Concerning the gas–solid reactions, the in situ observations and/or measurements by coupling the reaction systems with microscopic, spectroscopic, chromatographic or diffractometric analytic methods have highly contributed to better understanding of the kinetic behaviour of catalytic or non-catalytic reactions. For example, the gas–solid carbonation of alkaline sorbents has been usually studied by coupling thermogravimetric small reactors with gas chromatography

(GC) [1]. Recently, the Raman spectroscopy coupled to a reaction cell was used to investigate the carbon dioxide uptake by hydrated lime aerosol [2]. Environmental transmission electron microscopy (ETEM), environmental scanning electron microscopy (ESEM), infrared microscopy and synchrotron sources have also high potential to study directly the kinetic behaviour of gas–solid carbonation processes; but, these analytical techniques have not been used for this purpose to the best of our knowledge.

The gas–solid carbonation processes using alkaline sorbents are of growing interest because of their potential to capture and mineralize  $\text{CO}_2$  via non-catalytic exothermic reactions. This capture process allows the recovery of pure  $\text{CO}_2$  by a calcination (or de-carbonation) process performed at high temperature; this temperature is dependent on the nature of the produced carbonate [3–10]. Various alkaline sorbents have been proposed to capture and mineralize carbon dioxide ( $\text{CO}_2$ ) via gas–solid carbonation such as binary oxides (e.g.  $\text{CaO}$  and  $\text{MgO}$ ), hydroxides (e.g.  $\text{Ca}(\text{OH})_2$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{NaOH}$ ) and metastable powdered silicates (e.g.  $\text{Li}_2\text{SiO}_3$ ,  $\text{Na}_2\text{SiO}_3$ ,  $\text{CaSiO}_3$  and  $\text{MgSiO}_3$ ) [3–12]. On the other hand, the gas–solid carbonation of alkaline geo-particles takes

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**Fig. 1.** Portlandite mineral (reacting particles) characterized by platy nanoparticles (sheet forms), forming micrometric aggregates with high porosity. SEM-FEG micrographs obtained via secondary electrons.

place in various natural or artificial environments such as carbonates formation in unsaturated soils, in terrestrial or extraterrestrial aerosols, in cements/concretes, etc. (e.g. [2,13,14]).

In the present study, the powdered calcium hydroxide (or portlandite) was used as reactant for gas–solid carbonation process because this material is easily carbonated at low temperature and low  $\text{CO}_2$  pressure in presence of adsorbed water ( $0 < \text{water activity} < 1$ ). Moreover, this material is widely used in industrial and medical applications. For these carbonation experiments under variable environmental conditions, a reaction cell equipped with temperature and gas pressure controllers was coupled to an infrared microscope. Herein, we report on the role of initial adsorbed water, reaction mechanisms and kinetic modelling of  $\text{Ca}(\text{OH})_2$  carbonation.

### 1.2. $\text{Ca}(\text{OH})_2$ carbonation: role of adsorbed water

A substantial volume of the literature has revealed that gas–solid carbonation reactions are generally incomplete (carbonation efficiency  $< 80\%$ ) due to the formation of a protective carbonate layer around the reacting particles. In general, at low  $\text{CO}_2$  pressure ( $< 1$  bar), the carbonation efficiency of powdered sorbents depends mainly on the particle size, sorbent chemical structure, reaction temperature, fluid dynamics and relative humidity (e.g. [1–6,15,16]). For  $\text{Ca}(\text{OH})_2$  (portlandite) particles, Beruto and Botter [7] had clearly demonstrated that an increase of relative humidity catalyses the gas–solid carbonation and increases the carbonation efficiency up to 85% at constant low temperature ( $\approx 20^\circ\text{C}$ ) and low  $\text{CO}_2$  pressure ( $\approx 6.5$  mbar). These authors claimed that the  $\text{CO}_2$  pressure ( $< 1$  bar) has insignificant effect on the carbonation process at any relative humidity ( $< 90\%$ ). This assumption was later supported by Dheilly et al. [17]. This study has shown that under certain conditions (atmosphere with low level of  $\text{CO}_2$ , high relative humidity ( $\text{RH} = 100\%$ ) and low temperature ( $T = 10^\circ\text{C}$ )), the rate of carbonation is approximately 93% after 10 days. It reaches 100% after 25 days with a humid hydroxide. In the same context, our study proposes the in situ kinetic measurements of gas–solid car-

bonation of  $\text{Ca}(\text{OH})_2$  particles by using the infrared spectroscopy coupled to a reaction cell. These measurements provide complementary information on the carbonation kinetics and on the reaction mechanisms. For example, the hydroxide consumption and the water–carbonate formation can be directly and simultaneously monitored as a function of time. Moreover, the formation of metastable carbonate mineral phases such as aragonite, vaterite or hydrated carbonates can be also directly observed during gas–solid carbonation process.

## 2. Materials and methods

### 2.1. Starting reactants

#### 2.1.1. Synthetic portlandite or powdered calcium hydroxide ( $\text{Ca}(\text{OH})_2$ )

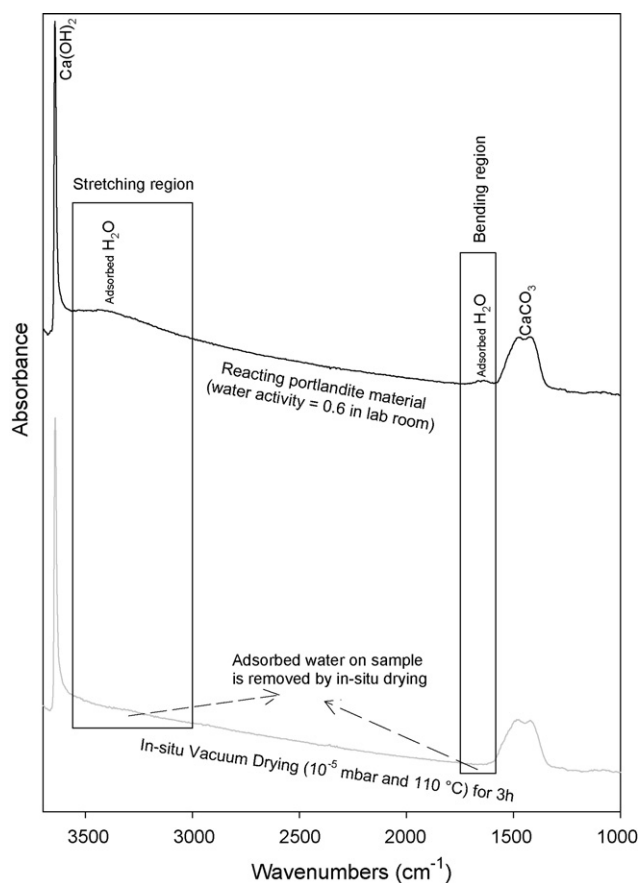
Portlandite material or calcium hydroxide  $\text{Ca}(\text{OH})_2$  was provided by Sigma–Aldrich with 96% of chemical purity, about 3% of  $\text{CaCO}_3$  and 1% of other impurities. The portlandite material is characterized by platy nanoparticles (sheet forms); forming micrometric aggregates with high porosity and/or high specific surface area (see Fig. 1). Moreover, this material contains a small amount of adsorbed water (or free molecular water) at atmospheric conditions, which is rapidly removed by using vacuum drying of samples ( $110^\circ\text{C}$  and  $10^{-5}$  mbar) (see Fig. 2). For the carbonation experiments, the portlandite was used without any physicochemical treatment.

#### 2.1.2. Carbon dioxide ( $\text{CO}_2$ )

Carbon dioxide  $\text{CO}_2$  was provided by Linde Gas S.A. with 99.995% of chemical purity. This gas was directly injected in the reaction cells without any treatment and/or purification.

### 2.2. Analytic procedure

An infrared microscope (BRUKER HYPERION 3000) coupled with a reaction cell (designed and built in our laboratory) was used in



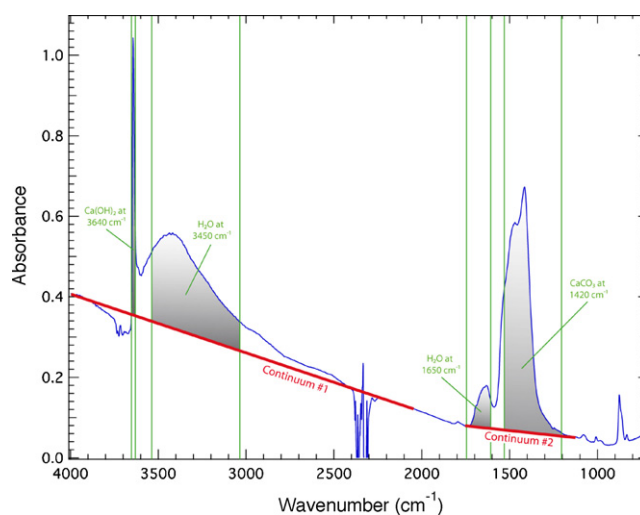
**Fig. 2.** Infrared measurements showed that reacting portlandite material contains a small amount of adsorbed water (water activity  $\approx 0.6$  in lab room), which is removed by in situ vacuum drying ( $10^{-5}$  mbar and  $110^\circ\text{C}$ ). The carbonate compound was also identified on this reacting material.

transmission mode. The detector was a MCT mono-detector cooled by liquid nitrogen. A spectral resolution of  $4\text{ cm}^{-1}$  was used for all measurements. The typical size of the infrared spot onto the sample was  $\sim 50\ \mu\text{m} \times 50\ \mu\text{m}$ . For these measurements, the reacting portlandite particles was manually deposited and compressed as a thin film on a KBr window. Then the KBr window was carefully placed in the reaction cell to be assembled to the microscope. For the gas–solid carbonation experiments in presence of adsorbed water (water activity  $\approx 0.6$  in lab room), 0.4, 1 or 1.5 bar of gas  $\text{CO}_2$  was directly injected in the reaction cell, i.e. without previous in situ vacuum drying of the sample. This means that the calcium hydroxide particles, stored at atmospheric conditions, were directly used for carbonation experiments. These particles contain small amount of adsorbed water or free molecular water (Fig. 2). From 6 to 10 infrared spectra were collected as a function of time until apparent equilibrium state (about 3 h). Conversely, for the dry solid–gas carbonation experiments, i.e. in absence of adsorbed water, the reacting sample was dried at  $110^\circ\text{C}$  and  $10^{-5}$  bar for 3 h using a heating system and a vacuum pump adapted to the reaction cell prior to  $\text{CO}_2$  injection. Here, 1 bar of  $\text{CO}_2$  was injected and two reaction temperatures were considered: 30 and  $300^\circ\text{C}$ .

Note that each carbonation experiment was repeated from 2 to 4 times in order to determine its reproducibility.

### 2.3. Calculation of integrated band intensities

The absolute intensities of the absorption bands were estimated by discrete integration between the band and a continuum defined below the band on a given wavenumber range. Let  $A(\lambda)$  be the



**Fig. 3.** Schematic representation for the calculation of integrated band intensities for each measured spectrum on the absorption bands of molecular  $\text{H}_2\text{O}$  at 1650 and  $3450\text{ cm}^{-1}$ , of carbonate group at  $1420\text{ cm}^{-1}$  and of hydroxide ion (OH) at  $3640\text{ cm}^{-1}$ .

absorption spectrum,  $C(\lambda)$  the continuum and  $\lambda_0$  and  $\lambda_1$  the respective low and high limits of the wavenumber range considered for the band intensity calculation. The absolute intensity of the band,  $I$ , is calculated as follows:

$$I = \sum_{i=\lambda_0}^{i=\lambda_1} A(i) - C(i) \quad (1)$$

This calculation of band intensity (Eq. (1)) was carried out for each measured spectrum on the absorption bands of molecular  $\text{H}_2\text{O}$  at 1650 and  $3450\text{ cm}^{-1}$ , of  $\text{CO}_3$  at  $1420\text{ cm}^{-1}$  and of  $\text{OH}^-$  at  $3640\text{ cm}^{-1}$  as represented on Fig. 3. The continuum was defined as linear segments on two different spectral ranges. Each of these segments is used to calculate the intensities of two different absorption bands (respectively  $\text{OH}^-$  and  $\text{H}_2\text{O}$  over segment #1 and  $\text{H}_2\text{O}$  and  $\text{CO}_3$  over segment #2). In both cases, the wavelength ranges used for the calculation of band intensities were defined in order to limit as much as possible the overlap between adjacent absorption bands.

## 3. Results and discussion

### 3.1. Gas–solid carbonation of portlandite in presence of adsorbed water

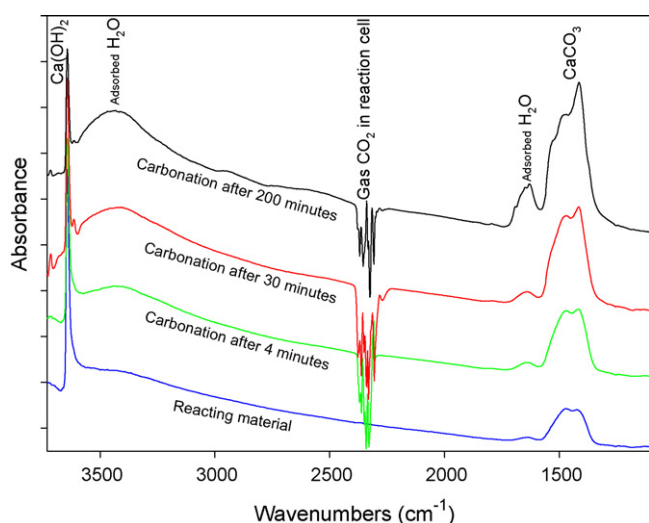
The experimental results have demonstrated that a slight amount of adsorbed water (free molecular water) on the calcium hydroxide particles allows the activation of the gas–solid carbonation reaction at low temperature ( $30^\circ\text{C}$ ). Here, we assumed a local production of carbonate ions ( $\text{CO}_3^{2-}$ ) at the gas–solid interfaces, allowing the carbonation process in the hydroxide external layer (or external surface area). We also assumed that this reaction was rapidly autocatalysed by the production of molecular water from the carbonation reaction, leading to the formation of a dense nonporous layer of carbonate (or protective carbonate layer) around the core of reacting particles (Fig. 4). Because, the infrared kinetic measurements shown in Fig. 4 have revealed an incomplete  $\text{Ca(OH)}_2$ – $\text{CaCO}_3$  transformation or incomplete gas–solid carbonation after 3 h of reaction, herein, the OH stretching vibration band ( $\nu_1$ ) at  $3642\text{ cm}^{-1}$  corresponding to the calcium hydroxide, was still detected in the carbonated particles at the apparent equilibrium state. Note also that the integrated band intensity for carbonate group at  $1420\text{ cm}^{-1}$  and the integrated band intensity for free-

**Table 1**

The kinetic behaviour of integrated band intensities for hydroxide ion at  $3640\text{ cm}^{-1}$ , molecular water at  $3450$  and  $1650\text{ cm}^{-1}$  and carbonate group at  $1420\text{ cm}^{-1}$  during solid–gas carbonation process.

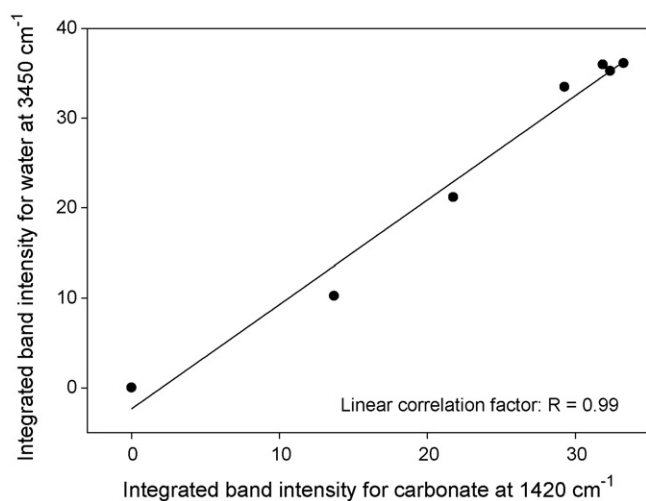
Reaction time, $t$ (min)	$A^{\text{OH}}$ at $3640\text{ cm}^{-1}$	$A^{\text{H}_2\text{O}}$ at $3450\text{ cm}^{-1}$	$A^{\text{H}_2\text{O}}$ at $1650\text{ cm}^{-1}$	$A^{\text{CO}_3}$ at $1420\text{ cm}^{-1}$
0	6.40	14.22	0.59	10.52
4	5.35	27.92	1.34	20.73
30	4.81	35.98	2.00	31.68
84	4.61	43.51	4.28	43.96
114	4.30	46.10	5.54	46.45
170	3.38	46.59	7.28	45.75
200	3.23	47.51	7.88	46.61

A: integrated band intensity.



**Fig. 4.** In situ kinetic measurements of gas–solid carbonation of portlandite ( $\text{Ca}(\text{OH})_2$ ) in presence of slight amount of adsorbed water (free molecular water) and at low temperature ( $30^\circ\text{C}$ ) using an infrared microscope coupled with a reaction cell.

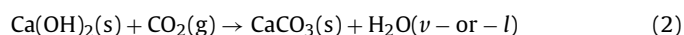
molecular- $\text{H}_2\text{O}$  stretching at  $3450\text{ cm}^{-1}$  increase proportionally with time during carbonation process until apparent equilibrium state (Fig. 5). This is clear evidence of equimolar production of molecular water and calcium carbonate in the system. The kinetic behaviour of integrated band intensities for hydroxide ion at  $3640\text{ cm}^{-1}$ , molecular water at  $3450$  and  $1650\text{ cm}^{-1}$  and carbon-



**Fig. 5.** Linear correlation between the integrated band intensities for molecular water at  $3450\text{ cm}^{-1}$  and carbonate at  $1420\text{ cm}^{-1}$  during solid–gas carbonation of  $\text{Ca}(\text{OH})_2$  particles.

ate group at  $1420\text{ cm}^{-1}$  during gas–solid carbonation process are reported in Table 1.

Globally, the gas–solid carbonation of portlandite particles can be expressed by the following exothermic reaction:



Theoretically, this means that the kinetic molar consumption of calcium hydroxide or carbon dioxide is directly proportional on the kinetic molar production of calcium carbonate or molecular water:

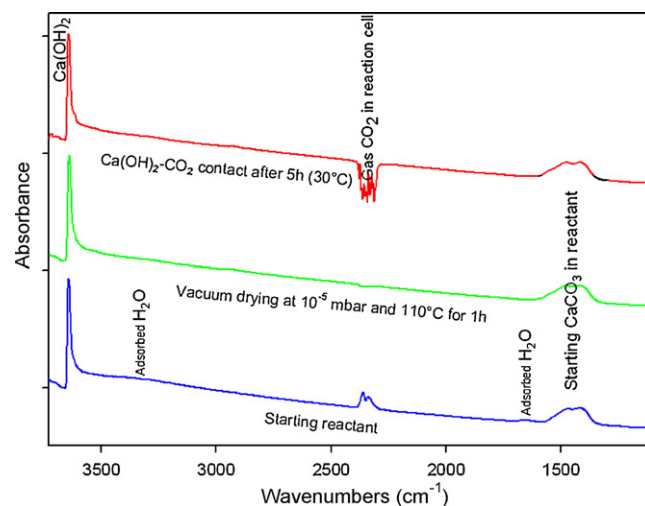
$$-\frac{dn_{\text{Ca}(\text{OH})_2,t}}{dt} = -\frac{dn_{\text{CO}_2,t}}{dt} = \frac{dn_{\text{CaCO}_3,t}}{dt} = \frac{dn_{\text{H}_2\text{O},t}}{dt} \quad (3)$$

Based on these above arguments, the variation of the OH consumption with time until apparent equilibrium allowed the calculation of relative extent of carbonation ( $\xi_c$ ) as a function of time by using the following equation:

$$\xi_c = \frac{A_i^{\text{OH}} - A_t^{\text{OH}}}{A_i^{\text{OH}}} 100 \quad (4)$$

where  $A_i^{\text{OH}}$  represents the initial integrated band intensity for OH stretching at  $3640\text{ cm}^{-1}$  and  $A_t^{\text{OH}}$  represents the integrated band intensity for hydroxide ion at instant time  $t$  (OH stretching at  $3640\text{ cm}^{-1}$ ). The OH consumption (or decay) and relative extent of carbonation ( $\xi_c$ ) as a function of time are reported in Table 2.

Conversely, the carbonation process at low temperature ( $30^\circ\text{C}$ ) was inhibited when the initial adsorbed water on the calcium hydroxide particles was removed from the system by in situ vacuum drying using a vacuum pump and a heating system adapted in the reaction cell ( $10^{-5}$  mbar,  $110^\circ\text{C}$ ) (see Fig. 6). This is a clear



**Fig. 6.** In situ infrared measurements show that the solid–gas carbonation of portlandite ( $\text{Ca}(\text{OH})_2$ ) in absence of adsorbed water, i.e. after vacuum-temperature drying at  $10^{-5}$  mbar and  $110^\circ\text{C}$  for 1 h is not detectable after 5 h of  $\text{Ca}(\text{OH})_2$ – $\text{CO}_2$  contact at low temperature ( $30^\circ\text{C}$ ).

**Table 2**The OH consumption (or decay) and relative extent of carbonation ( $\xi_c$ ) as a function of time.

Reaction time, $t$ (min)	$A^{\text{OH}}$ at $3640\text{ cm}^{-1}$	OH consumption (%) ( $A^{\text{OH}}/6.40$ ) $\times 100$	$\xi_c$ (%) Eq. (1)
0	6.40	100	0
4	5.35	83.54	16.46
30	4.81	75.13	24.87
84	4.61	71.97	28.03
114	4.30	67.25	32.75
170	3.38	52.80	47.20
200	3.23	50.45	49.55

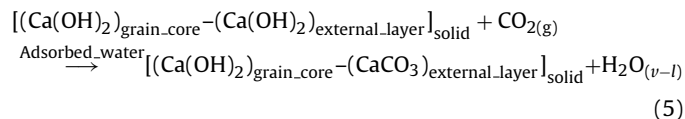
A: integrated band intensity;  $\xi_c$ : relative extent carbonation.

evidence of the catalytic role of adsorbed water at low temperature (<30 °C) and at low CO<sub>2</sub> pressure as demonstrated by early studies, e.g. [7,17]).

In summary, the carbonation reaction mechanism for calcium hydroxide in presence of adsorbed water can be explained by three steps:

- (1) Instantaneous activation step by the adsorbed water,
- (2) Autocatalytic step by the production of molecular water and,
- (3) Passivation step by the formation of a protective carbonate layer around the core of reacting portlandite particles.

Thus the carbonation reaction of calcium hydroxide can be expressed as:



In terms of efficiency, the carbonation process for these systems is incomplete (see Table 2). Physically, the formation of a dense nonporous layer of carbonate produces an increase of the volume at the grain scale (expansion or swelling process) or a decrease of porosity (pore closure process) whether porous materials are partially carbonated because the molar volume of carbonate mineral is higher than molar volume of calcium hydroxide (e.g. [7,9]). Concerning the nature of calcium carbonate formed during gas–solid carbonation experiments, a qualitative comparison of infrared spectra with calcite, aragonite and vaterite standards spectra, suggests the formation of complex calcium–carbonate mixture, mainly characterized by calcite, aragonite and possibly a hydrated calcium carbonate (see Fig. 7). The transitory metastable phases (aragonite and hydrated calcium carbonate) are transformed into the calcite after various days at atmospheric conditions or by in situ heating at 300 °C for 0.5 h, for this latter case, refer to Fig. 8. Note that the results shown in Figs. 7 and 8 with relevance to reaction mechanism of gas–solid carbonation of portlandite, had not been reported in the literature to the best of our knowledge.

### 3.2. Fitting of kinetic experimental-calculated data for gas–solid carbonation

A kinetic pseudo-second-order model was satisfactory used to fit the kinetic experimental-calculated data for gas–solid carbonation of calcium hydroxide in presence of adsorbed water. This model describes a fast mass transfer step (steps (1) and (2) cited above) followed by a slow equilibration of mass transfer. This last step is frequently interpreted as a diffusion process. Here, we interpret it as a passivation process (step (3)) due to the formation of a protective carbonate layer around the core of reacting particles. The

differential form for this kinetic model can be written as follows:

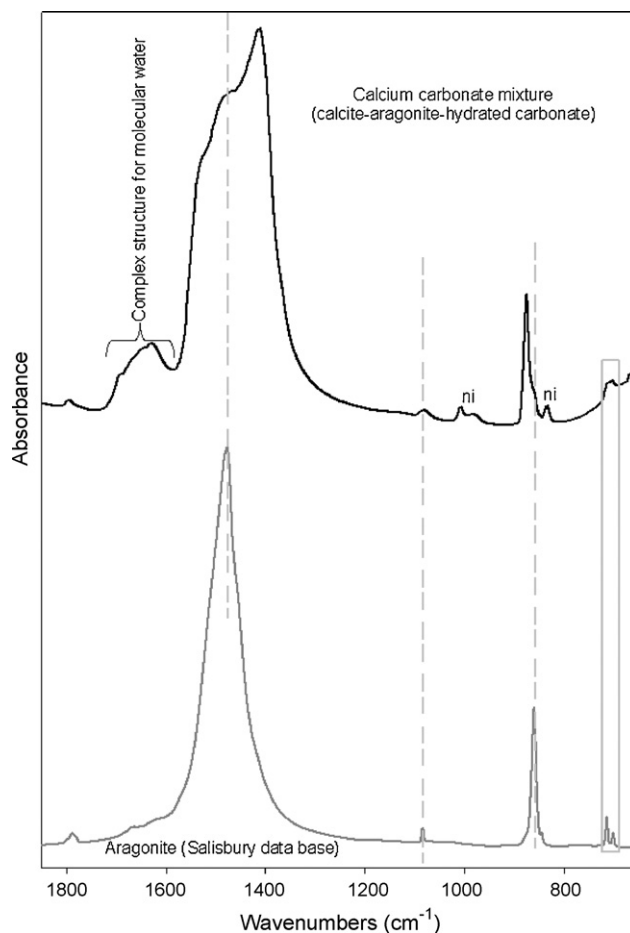
$$\frac{d\xi_{c,t}}{dt} = k_c(\xi_{c,\text{max}} - \xi_{c,t})^2 \quad (6)$$

where  $k_c$  is the rate constant of Ca(OH)<sub>2</sub> carbonation [1%/min],  $\xi_{c,\text{max}}$  is the maximum relative-extent of carbonation at equilibrium [%],  $\xi_{c,t}$  is the relative extent of carbonation at any time,  $t$  [%] (see Eq. (4)).

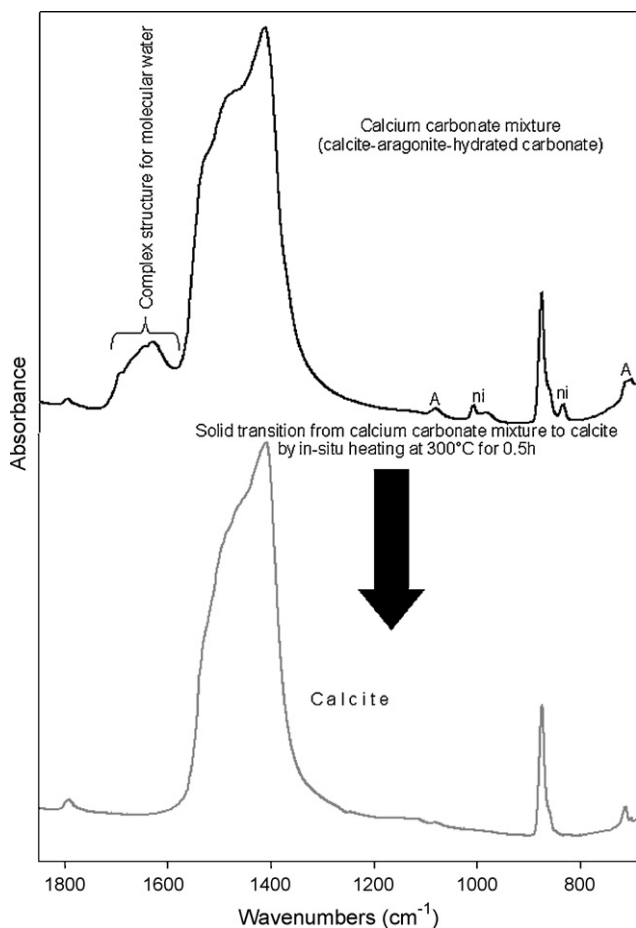
The integrated form of Eq. (6) for the boundary conditions  $t=0$  to  $t=t$  and  $\xi_{c,t}=0$  to  $\xi_{c,t}=\xi_{c,t}$ , is represented by a hyperbolic relationship:

$$\xi_{c,t} = \frac{\xi_{c,\text{max}}t}{(1/k_c\xi_{c,\text{max}}) + t} \quad (7)$$

Remark that the rate constant  $k_c$  (1%/min) has no physical interpretation. For this reason a new parameter can be defined



**Fig. 7.** Calcium carbonate formed via gas–solid carbonation of portlandite after 200 min, it is characterized by complex carbonate mixture of calcite, aragonite and possibly hydrated carbonate. Aragonite reference from Salisbury data base [18], ni: not identified.



**Fig. 8.** Solid transition from calcium carbonate mixture to calcite by in situ heating at 300 °C for 0.5 h. A: aragonite, ni: not identified.

“(1/k<sub>c</sub> × ξ<sub>c,max</sub>) = t<sub>1/2</sub>”, which, represents the duration after which half of the maximum relative-extent of carbonation was obtained. In the current study, t<sub>1/2</sub> is called “half-carbonation time” and can be used to calculate an initial relative rate of carbonation, ν<sub>0,c</sub>, [%/min] by using the following expression:

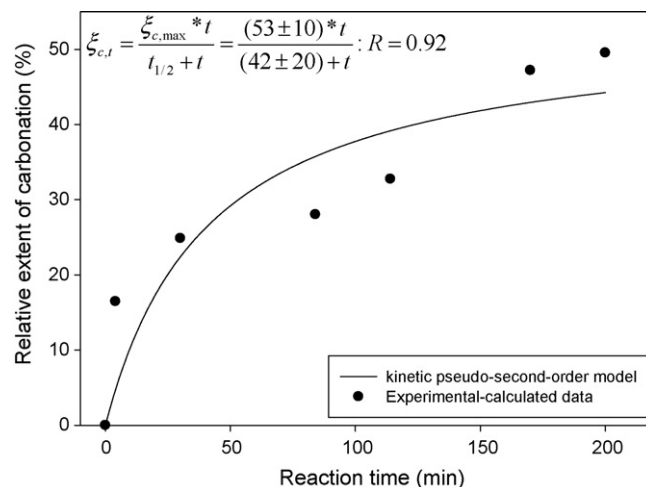
$$\nu_{0,c} = \frac{\xi_{c,\max}}{t_{1/2}} = k_c(\xi_{c,\max})^2 \quad (8)$$

Graphically, the initial relative rate of carbonation ν<sub>0,c</sub> is defined as the slope of the tangent line when the time *t* tends towards zero on the ξ<sub>c,t</sub> vs. *t* curve.

The fitting of kinetic data (ξ<sub>c,t</sub> vs. *t*) by using Eq. (7) allows the estimation of t<sub>1/2</sub> and ξ<sub>c,max</sub> parameters. A non-linear regression by the least-squares method was performed (see Fig. 9). The fitting parameters (t<sub>1/2</sub> and ξ<sub>c,max</sub>), the initial relative rate of carbonation (ν<sub>0,c</sub>) (calculated by Eq. (8)) and the correlation factor values are directly reported in Fig. 9. In general, the prediction of maximum relative-extent of carbonation is in agreement with experimental-calculated data. Unfortunately, a high numerical error was estimated on the half-carbonation time parameter. This could be due to a non-continuous passivation step during carbonation process.

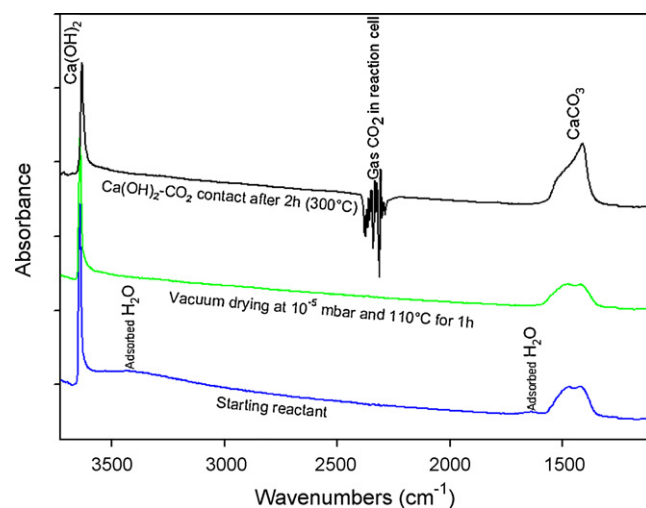
### 3.3. Gas–solid carbonation of calcium hydroxide in absence of adsorbed water

As mentioned in Section 3.1, the carbonation process at low temperature (30 °C) was inhibited when the initial adsorbed water on the calcium hydroxide particles was removed from the system by



**Fig. 9.** Kinetic modelling of gas–solid carbonation for calcium hydroxide in presence of adsorbed water was performed using a pseudo-second-order model. Here, a non-linear regression by the least squares method was used.

in situ vacuum drying (10<sup>−5</sup> mbar, 110 °C) (see Fig. 6). Conversely, the calcium hydroxide was slightly carbonated at 300 °C (Fig. 10). In fact, the calcium hydroxide can be significantly carbonated via dry gas–solid reaction at higher temperature and preferentially when this material is completely dehydrated, i.e. transformed to calcium oxide (CaO). Here, the carbonation temperatures are typically (>600 °C) [16]. The reaction mechanism for dry gas–solid carbonation has been rarely discussed in the literature. Here, we assumed that a atomic excitation at high temperature is necessary, allowing to the migration of oxygen atom from the solid towards adsorbed gaseous CO<sub>2</sub> and then producing its mineralization in carbonate around the core of the grains. Then, the formation of a dense nonporous layer of carbonates around the core of the grains take places and produces a passivation process due to a blocking of intra-particle diffusion of CO<sub>2</sub> inside the core of the reacting grains. Conceptually, this step is similar to the passivation step described for solid–gas carbonation process in presence of adsorbed water.



**Fig. 10.** In situ infrared measurements revealed a slight solid–gas carbonation of portlandite (Ca(OH)<sub>2</sub>) at 300 °C when the initial adsorbed water was previously removed from the system, i.e. after vacuum-temperature drying at 10<sup>−5</sup> mbar and 110 °C for 1 h.

#### 4. Conclusion

In this study, we demonstrated that the in situ kinetic measurements by using infrared spectroscopy coupled with a reaction cell provide complementary information with relevance to the reaction mechanism and kinetic behaviour of gas–solid carbonation of calcium hydroxide (portlandite). Here, the hydroxide consumption and the water–carbonate formation were directly and simultaneously monitored as a function of time. Moreover, the formation of metastable aragonite was identified and hydrated calcium carbonate was suspected during carbonation process.

This study also demonstrated that gas–solid carbonation of calcium hydroxide is activated at low temperature (<30 °C) and low CO<sub>2</sub> pressure (<1.5 bar) by free molecular water adsorbed on the surface of reacting particles. If the solid–gas carbonation of calcium hydroxide particles cannot be activated at low temperature in absence of adsorbed water, this “dry route” seems efficient at higher temperature (300 °C) and low CO<sub>2</sub> pressure (<1 bar). In this case, we make the hypothesis that the atomic excitation at high temperature enables the migration of oxygen atoms from the solid towards adsorbed CO<sub>2</sub>, producing its mineralization as carbonate around the core of the grains.

#### Acknowledgements

The authors are grateful to the University Joseph Fourier-Grenoble 1, (Terre, Univers, Environnement, Société “TUNES” post-doctoral program) for providing the financial support.

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