Role of hydrate phases of calcium carbonate on the scaling phenomenon

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Abstract

The existence of a metastable field in the precipitation of calcium carbonate is an experimental fact. Indeed, the saturation in relation to the different anhydrous forms of $CaCO_3$ (calcite, aragonite and vaterite) is often extensively passed without any precipitation occurring. Through experimental exploration of the metastable field by the LCGE method and the use of new thermodynamic data of $CaCO_3$ hydrated forms, a new diagram of thermodynamic evolution of the calco-carbonic system has been validated. Above 20°C, the solubility product of calcium carbonate monohydrate (MCC) constitutes a necessary lower limit for deferred spontaneous germination. In contrast, precipitation with homogeneous predominance will happen instantaneously when the solubility product of amorphous calcium carbonate (ACC) is reached. When the ionic activity product of the solution, $(Ca^{2+})(CO_3^{2-})$, stabilizes between solubility products of monohydrated and amorphous forms, the germination time and the precipitation kinetics highly depend on the wall nature. Germination can only be predominantly heterogeneous. These two hydrated forms (ACC and MCC) constitute precursors to $CaCO_3$ precipitation. They are very unstable and are quickly transformed to give the anhydrous forms of calcium carbonate.

Keywords: Hydrated calcium carbonate; Scaling; Germination; Metastable state

1. Introduction

The overtaking of the solubility product is a necessary condition to the formation of a solid phase, but experience in the laboratory [1,2] as well as in natural habitats [3] shows that this is

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not sufficient. Solutions supersaturated in calcium carbonate can preserve this state without any apparition of crystals: this is the metastable state.

In a recent publication [4] we demonstrated the existence of a precipitation straight limit (PSL). The PSL corresponds to the sites of germination points in the plan $\{[Ca], \log(pCO_2)\}$,

of calco-carbonic solutions stripped with atmospheric air. This allows definition of the metastable zone as the zone of supersaturation located between the PSL and the equilibrium curve of the least soluble variety of $CaCO_3$, which is calcite. This line constitutes a very important tool of scaling prevention since it defines limit conditions over which the formation of tartar intervenes. But can this PSL provide a knowledge tool for the calco-carbonic system?

Some experimental data, obtained frequently and continuously, can provide a coherent interpretation. We particularly have observed spherical or spheroid shapes [5] during the passage to the SEM of deposits collected. This precipitate evidently belonged to no crystallized form of calcium carbonate. In a recent work, Gache [6] had identified similar structures obtained by double decomposition (mixture solutions of $CaCl_2$ and Na_2CO_3) as being $CaCO_3H_2O$. Ogino et al. [7] had synthesized amorphous $CaCO_3$ that precipitated under spherical particles. It seems that these structures are consolidated by the presence of the Mg^{2+} ions or by inhibitors as aminopolyphosphate acid.

The purpose of this work is to try to improve the mechanisms of the precipitation. $CaCO_3$ mineralogy and its thermodynamic data will be taken into consideration to clarify the role of hydrated forms in the germination of calcium carbonates.

2. Method and tools

This technique (LCGE [8]) aims at the dissociation of the different kinetic stages to isolate the most limiting one that is often the mass transfer on the solid liquid interface. Let's recall that this method consists of displacing the equilibrium of the $Ca(HCO_3)_2$ solution by stripping it with a mixture CO_2–air. The CO_2 partial pressure of the stripping gas is lower than the equilibrated pCO_2 [Eq. (1), 9]) of the calco-
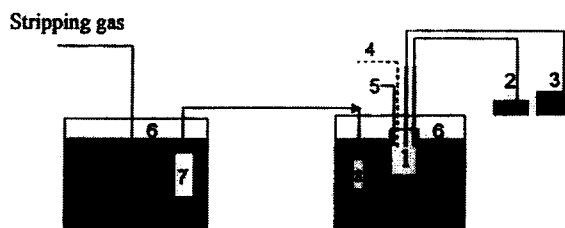

Fig. 1. Experimental installation. 1 work cell; 2 pH meter; 3 quartz crystal microbalance; 4 sample taken for dosage of [Ca]; 5 support to trap the precipitate (for SEM); 6 thermostat baths; 7 humidifier; 8 humidity trap.

carbonic solution. In this way supersaturation is created. The amplitude of the supersaturation can be adjusted according to the initial concentration of the solution, the pCO_2 of the stripping gas and the temperature. The evolution of pH and [Ca] is followed along the experiment. The pCO_2, the IAP and the supersaturation of the solution are determined by a calculation code. The deposited crystals are collected on a trap and identified by a scanning electronic microscopy (SEM). The addition of a quartz crystal microbalance allows following the reaction on the solid (sensor) immersed in the solution. A calco-carbonic solution is prepared by the stripping of pure CO_2 in an aqueous suspen-sion of $CaCO_3$.

$$pCO_2 = \frac{D \cdot TA \cdot 10^{K_1 - pH}}{\dfrac{2.10^{pH - K_2}}{f_{CO_3^2}} + \dfrac{1}{f_{HCO_3^{1-}}}}$$

where $TA = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-]$; for pure calco-carbonic solution: $TA \approx 2[Ca^{2+}]$.

3. Crystallographic varieties of calcium carbonate

Most research on calcium carbonate has dealt with anhydrous crystalline polymorphs (calcite

Table 1
Logarithmic solubility products for the various forms of calcium carbonate

Varieties	Equations of pKs (T in K and t in °C)		Reference
Calcite	$171.9065 + 0.077993.T - 2839.319/T - 71.595.\log(T)$	$0 < t < 90°C$	12
Aragonite	$171.9773 + 0.077993.T - 2903.293/T - 71.595.\log(T)$	$0 < t < 90°C$	12
Vaterite	$172.1295 + 0.077996.T - 3074.688/T - 71.595.\log(T)$	$0 < t < 90°C$	12
ACC	$6.1987 + 0.0053369.t + 0.0001096.t^2$	$10 < t < 55°C$	13
$CaCO_3,H_2O$	$7.05 + 0.000159.t^2$	$10 < t < 50°C$	10
$CaCO_3,6H_2O$	$2011.1/T - 0.1598$	$0 < t < 25°C$	11

aragonite and vaterite). The hydrate forms have been much less examined, probably because of their low stability. The expressions of logarithmic thermodynamic solubility products (or equilibrium constants) for all the varieties of $CaCO_3$ are given in Table 1.

• Amorphous calcium carbonate (ACC): It is the most instable form, and is often described in spherical shapes of diameter lower than a micrometer. The ACC initially formed is transformed within a few minutes to a mixture of severe crystalline of calcium carbonates. The transformed carbonates are vaterites and calcites at low temperatures (14–30°C) and aragonites and calcites at high temperatures (60–80°C). At intermediate temperatures (40–50°C) the formation of all three varieties was observed [3].

• Monohydrate calcium carbonate (MCC) [10]: It crystallizes in a hexagonal system under spheroid shapes. The synthesis of this mineral required the presence of magne-sium and of some other ions (seawater constituents) as well as organic material.

• Hexahydrate calcium carbonate (HCC): Both in nature and in the laboratory the mineral readily crystallizes (in a monoclinic system) at a temperature near 0°C, yet rapidly decomposes to anhydrous forms at warmer temperatures [11].

4. Results and discussion

In a recent work [14] we described a certain number of tests to specify the physical significance of the precipitation straight limit (PSL). Let's recall that the PSL corresponds to the sites of germination points in the plan {[Ca], $\log(pCO_2)$} for calco-carbonic solutions stripped with atmospheric air. The partial pressure of the CO_2 at the germination moment was determined by following the evolution of pCO_2 vs. [Ca^{2+}], as shown in Fig. 2. Values of the pCO_2 are calculated by a code using the applied data (pH, [Ca]).

At 30°C, the PSL was determined for calco-carbonic solutions with concentrations over 1.5 mmol.L^{-1}. Indeed, there is no precipitation (after 1900 min) when 1 mmol.L^{-1} calco-carbonic solution is stripped with atmospheric air ($pCO_2 = 3 \times 10^{-4}$ atm). However, when the same solution was stripped with synthetic air ($pCO_2 = 5 \times 10^{-5}$ atm), precipitation occurred after about 100 min. The pCO_2 at the germination moment is much lower than the values of the PSL (Fig. 3). Therefore, a PSL displacement is possible at low concentrations if the pCO_2 of the stripping gas is lower than the one of atmospheric air.

Hence it becomes important to study the possible displacement of the PSL position. Experiments to determine the PSL at 30°C, 50°C
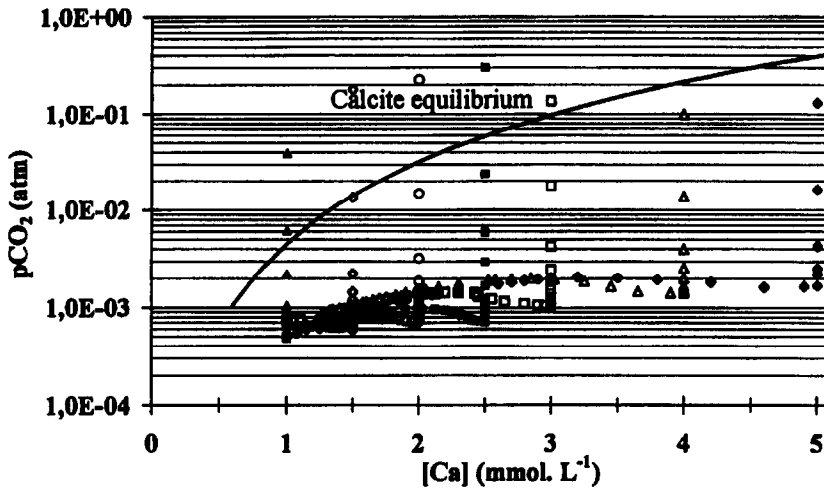
Fig. 2. Evolution of pCO_2 of calco-carbonic solutions stripped with atmospheric air at 30°C.
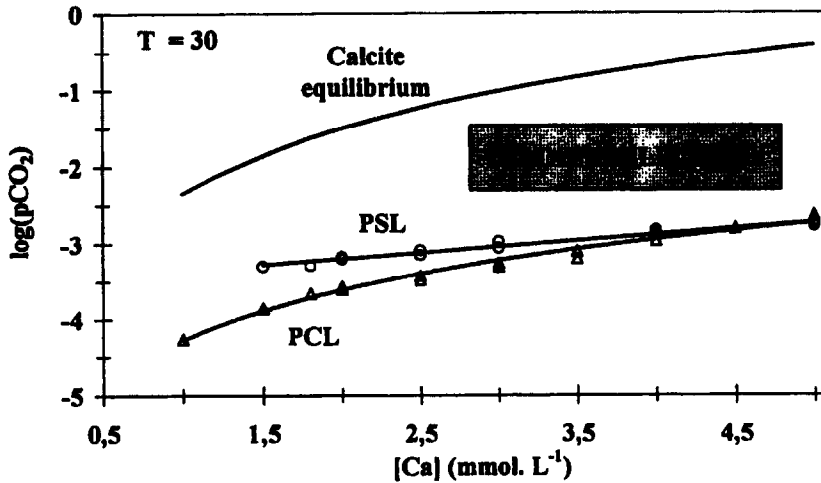

Fig. 3. Metastable zone and comparison of the PCL position with the PSL one (germination points).

and 60°C were redone while using synthetic air. Results shown in Fig. 3 provide a logarithmic relation in the plan {[Ca], log(pCO_2)} between the different observed germination points. By analogy to the PSL, this curve is called the precipitation curve limit (PCL). To better explain this phenomenon, we compare the position of the PCL and the PSL with the equilibrium curves of all $CaCO_3$ varieties, as shown in Fig. 4. It clearly

appears that the PSL is located between equilibrium curves of amorphous $CaCO_3$ and $CaCO_3$, H_2O, whereas the PCL corresponds, within the applied mistakes, to the equilibrium curve of the ACC. We often observed that there is no spontaneous precipitation when the IAP of the calco-carbonic solution did not reach the solubility product of $CaCO_3,H_2O$.

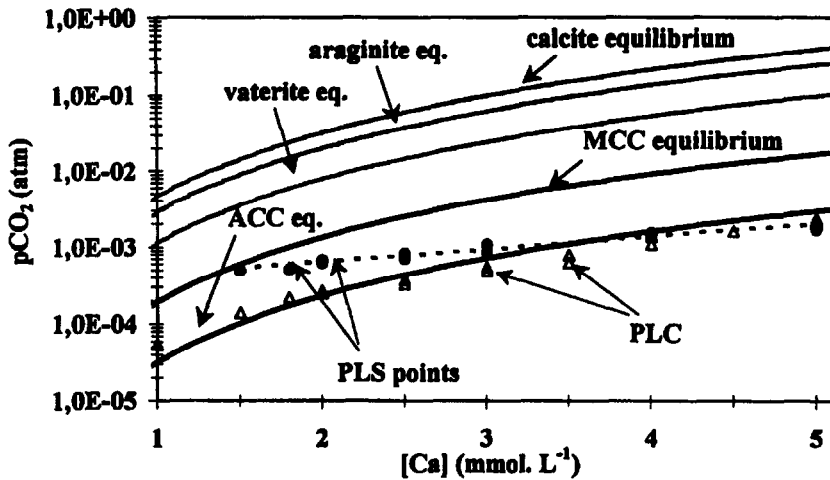Some research on $CaCO_3$ characterization

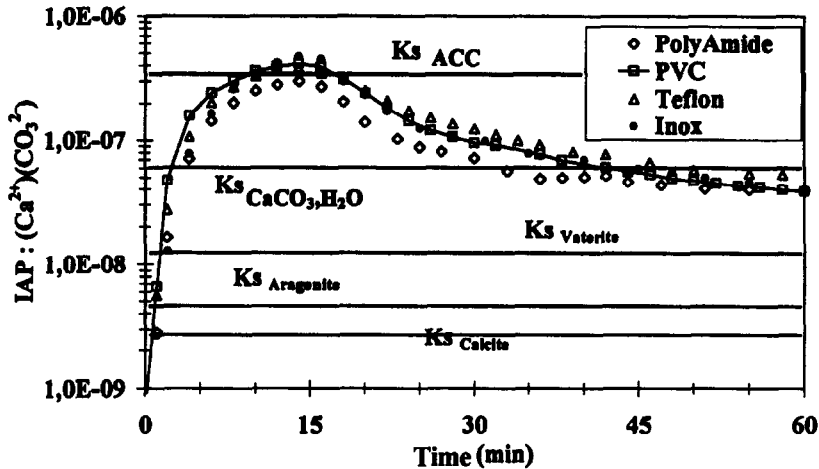Fig. 4. Comparison of PCL and PSL positions with equilibrium curves of $CaCO_3$ varieties.

Fig. 5. Evolution of the IAP in relation to solubility products of the different varieties of $CaCO_3$ and for four types of cells ($[Ca^{2+}] = 4$ mmol. L^{-1}, $T = 30°C$.

[3,15], synthesized by double decomposition (highly supersaturation solutions of $CaCl_2$ and alkaline carbonate), affirm a precursor role of hydrated forms in the germination of calco-carbonic system. These observations motivated us to evaluate the precursor roles of the ACC and MCC in the scaling phenomenon.

4.1. Precursor roles of amorphous and mono-hydrated forms in $CaCO_3$ germination

We studied the possibilities and conditions of the existence of one of these precursors in our tests using the LCGE technique. The evolution of the IAP was compared to solubility products (Ks)

of the different varieties of $CaCO_3$ found in the literature. All the experimental results of the $CaCO_3$ precipitation can be classified into three categories:

- IAP_G reaches the Ks of amorphous $CaCO_3$
- $Ks_{MCC} < IAP_G < Ks_{ACC}$
- IAP stabilizes at a value lower than the Ks of $CaCO_3, H_2O$

4.1.1. Case where the solubility product of the ACC is reached

The chosen example ($[Ca^{2+}] = 4$ mmol.L^{-1}, $T = 30°C$) corresponds to a series of experiments for four types of cells where points of germination belong to the PCL. Fig. 5 shows that in all tests the solubility product of the ACC is reached and the precipitations are released instantaneously and independently of the nature of the cell.

Solubility products of the four varieties are passed without any germination occurring. On the contrary, as soon as the solubility product of ACC is reached, the precipitations are released with almost identical kinetics.

Under these conditions (solution saturated with amorphous $CaCO_3$; $\Omega_{ACC} \approx 1$), the germination time (T_G), granted by pH and [Ca], is practically the same. QCM intervenes simultaneously with the other signals of germination, as shown in Table 2.

4.1.2. Case where the IAP_G is located between solubility products of the ACC and MCC

The second chosen example ($[Ca^{2+}] = 2.5$ mmol.L^{-1}, $T = 30°C$) corresponds to a series of experiments where points of germination belong to the PSL and not to the PCL. Fig. 6 shows that the IAP overtakes the solubility product of the monohydrate form without reaching the amorphous one. Thereafter, different germinations are released. The IAP_G is practically constant, but the germination times are very much influenced by the wall nature.

Perceptions of germination time granted by pH and [Ca] have a tendency to differ, but especially the QCM is found to be more or less greatly displaced. All of these signals become overly sensitive to the wall nature as shown in Table 2.

Table 2
Comparison of germination signal values vs. supersaturations and cell natures

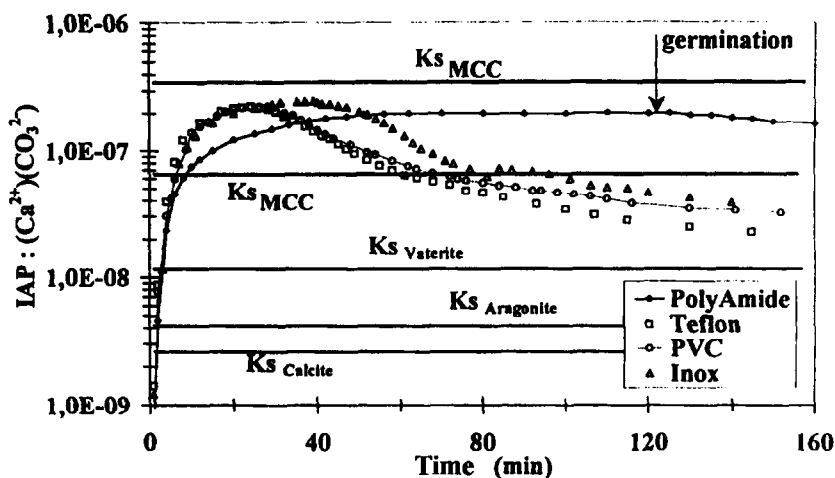|	[Ca] mmol.L^{-1}	Ω_{ACC}	Ω_{MCC}	T_G(/pH), min	T_G(/[Ca]), min	T_G(/QCM), min
PVC	4	1.20	6.5	14	14	14
	3	0.77	4.2	22	22	24
	2.5	0.63	3.4	30	32	40
Teflon®	4	1.10	5.9	14	14	14
	3	0.78	4.2	20	21	22
	2.5	0.67	3.6	26	28	34
Inox	4	1.17	6.4	14	14	14
	3	0.87	4.7	24	25	28
	2.5	0.69	3.7	39	42	52
Polyamide	4	0.97	5.3	14	14	14
	3	0.76	4.2	44	46	55
	2.5	0.58	3.2	125	130	>300

Fig. 6. Evolution of the IAP in relation to solubility products of the different varieties of $CaCO_3$ and for four types of cells ($[Ca^{2+}] = 2.5$ mmol. L^{-1}, $T = 30°C$).

To summarize, when the IAP of the calco-carbonic solution stabilizes between solubility products of monohydrate and amorphous forms, germination becomes much slower. A decrease of pH begins to appear before the precipitation. A gap also appears between the germination time granted by pH or [Ca] and the time of the QCM. The gap amplitude, the germination time and the precipitation kinetics highly depend on the wall nature. This phenomenon is very accentuated when the IAP of the solution does not move away sufficiently from the solubility product of $CaCO_3,H_2O$.

Because of its marked dependence on the nature of the wall, germination can only be with heterogeneous predominance. On the contrary, in the case where the solubility product of the ACC is reached, all of these signals characterizing precipitation intervene simultaneously and independently of the wall nature. Germination seems to be with homogeneous predominance.

4.1.3. Case where the solubility product of the $CaCO_3,H_2O$ is not reached

In the experiment presented in Fig. 7, a calco-carbonic solution ($[Ca^{2+}] = 4$ mmol. L^{-1}, $T = $ 30°C) was first stripped by gas with high CO_2 partial pressure ($1.05×10^{-2}$ atm). The IAP stabilized at a value slightly lower than the solubility product of the monohydrated form. Germination did not take place after 170 min (in another experiment 600 min). The experiment was continued but with atmospheric air ($pCO_2 = 4×10^{-3}$ atm) as stripping gas. The pH increased again, and thereafter the IAP also increased, which had reached the value of the ACC solubility product after a few minutes. Then the precipitations were released instantaneously and the IAP decreased quickly.

This example confirms that precipitation is instantaneous as soon as the solubility product of the amorphous form is reached. Contrarily, the precipitation did not occur after a relatively long time where the solubility product of $CaCO_3,H_2O$ was not overtaken.

In another case ($[Ca^{2+}] = 1$ mmolL^{-1}, $T=30°C$ and $pCO_2=4×10^{-4}$ atm), precipitation did not occur after 1900 min. The solution was supersaturated in relation to the three anhydrous forms (calcite, aragonite and vaterite) but undersaturated in relation to the two hydrated ones (MCC and ACC). Thus, $CaCO_3,H_2O$ seems to

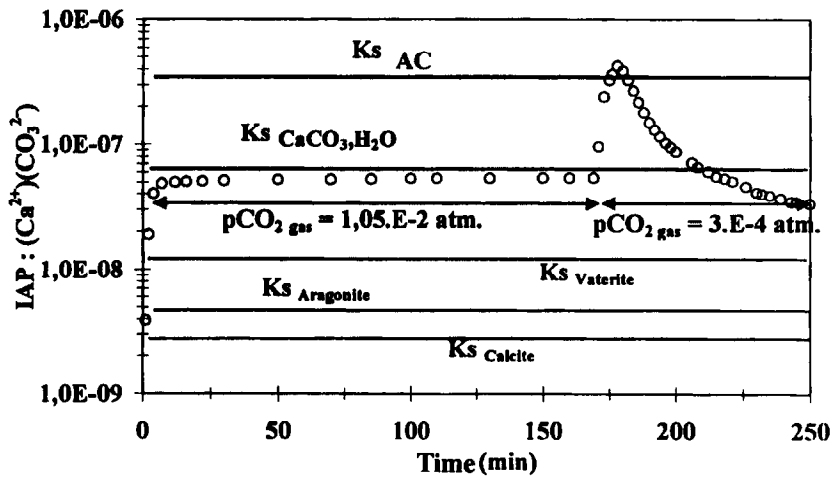Fig. 7. IAP evolution for a solution stripped with two gases ([Ca^{2+}] = 4 mmol. L^{-1}, T = 30°C).

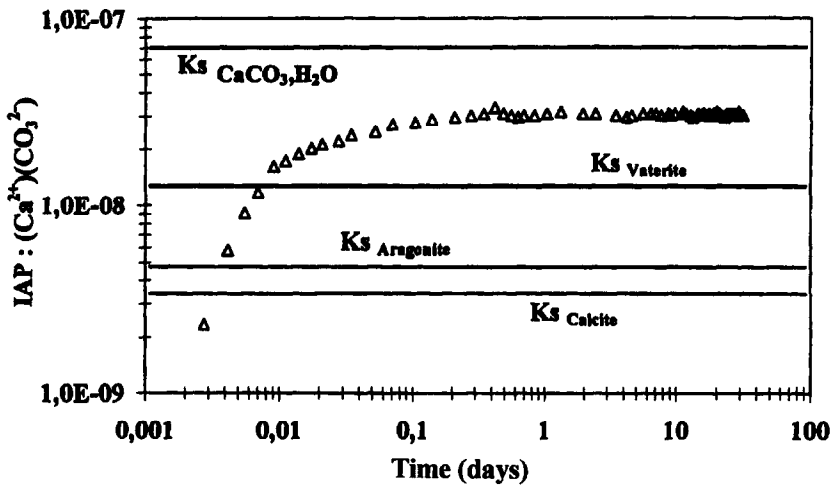Fig. 8. Stability of IAP solution between the solubility products of the vaterite and $CaCO_3H_2O$ after 31 days.

really represent the limit of the metastable zone over which the precipitation is possible after a longer germination time.

Can we confirm that the precipitation will not take place if the Ks of the $CaCO_3H_2O$ is not reached? In this sense, a long-term experiment was made. The applied conditions were chosen so that the target IAP of the solution was located between the MCC solubility product and the

vaterite one. The test took place under conditions permitting the stability of the solution after a long stripping time. These conditions are:

- calco-carbonic solution with [Ca^{2+}] = 1.2 mmol. L^{-1}
- temperature equal to 25°C (nearing the ambient temperature)
- stripping gas: atmospheric air

The experiment was carried out for 31 days without any precipitation occurring, as shown in Fig. 8. Indeed, as had been predicted, the IAP of the solution was consolidated after about 10 min between solubility products of vaterite and $CaCO_3,H_2O$.

Thirty-one days represent an almost infinite time either on the laboratory ladder or the industrial and atmospheric cooling one. Thus, the confirmation that $CaCO_3,H_2O$ represents the limit of metastability state of a calco-carbonic system becomes more and more obvious. Monohydrate calcium carbonate thermodynamic data should be taken into consideration in scaling problems.

5. Conclusions

Ogino et al. [3], who were among the first ones to use ACC thermodynamic data, proved the existence of ACC at highly supersaturation solution. Clarkson et al. [15] affirmed the role of $CaCO_3,6H_2O$ as a precursor for calcium carbonate precipitation at low temperature. Lately, Gal et al. [16] confirmed the precursor role of ACC and MCC using the critical pH method.

Interpretation of the results allowed to develop the scaling process mechanisms. An embryonic interpretation of the metastability zone has been proposed and confirmed the major role played in $CaCO_3$ precipitation by the amorphous and monohydrated forms.

The PSL position between equilibrium thermodynamic curves of these two hydrated forms led to a coherent analysis of a multitude of experimental data accumulated by several generations of researchers. It leads to a satisfactory synthesis represented in abbreviated form in Table 3.

The MCC solubility product constitutes a lower limit needed for spontaneous germination in the calco-carbonic system. Thus, predicting scaling should consider the $CaCO_3,H_2O$ and not the most stable thermodynamic one (calcite).

Table 3
Data from experiments

$Ks_{CCM} < IAP_G < Ks_{CCA}$	Ks_{CCA} is reached
Precursor: $CaCO_3,H_2O$	Precursor: Amorphous $CaCO_3$
Low supersaturation in relation to calcite	High supersaturation in relation to calcite
Slow germination	Rapid precipitation
pH pseudo-landing before germination	pH pick at the moment of germination
QCM respond after the germination moment	QCM respond at germination moment
Results often non-reproducible	Results often reproducible
Wall nature dependence	Wall nature independence
Predominantly heterogeneous germination	Predominantly homogeneous germination

6. Symbols

D — Henry's law coefficient (≈ 33.2 atm L mol^{-1} at 30°C)

[Ca] — Concentration of Ca^{2+}

f — Activity coefficient

G — Index for the germination moment

IAP — Ionic activity product $(Ca^{2+})(CO_3^{2-})$

K_1, K_2 — First and second constant dissociation of carbonic acid

Ks — Solubility product

QCM — Quartz crystal microbalance

pCO_2 — Partial pressure of CO_2 (in atm; 1 atm = 1.01×10^{-5} Pa)

Greek

Ω — Supersaturation ($\Omega = IAP/Ks$)

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