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Calcium Sulfate and Calcium Carbonate Simple and Mixed Precipitations

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Abstract - This study focuses on calcium sulfate (gypsum) and calcium carbonate (CaCO_3) simple and mixed precipitations. These forms of scaling are still an issue in several industrial applications such as cooling towers and water desalination, either by thermal-based or membrane-based processes. CaCO_3 precipitation has been studied by the degassing method while the gypsum simple and mixed precipitations have been studied by the double decomposition method, and by following 4 parameters simultaneously, namely: pH and total alkalinity serve to detect the CaCO_3 precipitation, calcium ion concentration allows following the gypsum germination, and the quartz crystal microbalance (QCM) response gives information about the salts seeding, especially gypsum. A kinetic study of CaCO_3 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ mixed precipitation resulted in a different form to that of the simple precipitation. Indeed, even though the pH remains the key parameter to detect CaCO_3 precipitation either under simple or mixed precipitation forms, as the QCM response was found not to be a good parameter to detect the CaCO_3 germination in a mixed system, especially when it precipitates after calcium sulfate, the QCM response remains a specific parameter to gypsum crystals because even after the appearance of the first CaCO_3 crystals, gypsum germination continues with faster kinetics. Gypsum germination time in co-precipitation is higher than that corresponding to the simple precipitation ($\text{CaSO}_4\text{-H}_2\text{O}$ system) because of the competition between the different co-precipitating ions.

Key words: Scaling / Simple and mixed precipitations / Germination / Degassing / Double decomposition.



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1. Introduction

Scaling, a frequent phenomenon occurring in water distribution pipes and some industrial applications such as cooling towers and water desalination, either by thermal-based or membrane-based processes (Waly et al. 2012; Ghaffour et al. 2013), is characterized by the appearance of an adhering crystalline deposit constituted essentially by calcium carbonate (CaCO_3) and gypsum, amongst other scaling forms, on the pipes, distillers' walls or on membranes surfaces (Bernard and Pascal 1960; Powel et al. 1964; Amathieu 1985; Ghorbel et al. 1991; Rola 1994; Gal et al. 1996; Sheikholeslami 2000; Sheikholeslami 2003; Arras et al. 2009; Rahmawati et al. 2012).

Crystallization, mainly kinetic and thermodynamic aspects, has been widely studied for many years (Sohnel and Mullin 1988; Mullin 1993; Elfil and Roques 2001; Alimi and Elfil 2003; Elfil and Roques 2004; Elfil 2006; Elfil et al. 2007) and exhaustive information is available in literature for pure salts, mainly CaCO_3 and calcium sulfate dehydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which are the major scaling contributors (Marshall and Slusher 1966; Elfil and Roques 2001). In fact, recent studies have been interested to the possibility of controlling or reducing this problem by several methods, mainly chemical treatment (Xyla et al. 1992; Gal et al. 1996; Barrett and Parsons 1998; Elfil and Nawel 2004; Szczes 2008; Wu et al. 2010). There are also a number of alternative non-chemical treatment options available for scaling control. Amongst these is the use of magnetic, electronic and electrolytic treatment devices (MacAdam and Parsons 2004; Al Nasser et al. 2011). Each of these scale controlling methods has its advantages and a number of factors need to be considered before choosing the right option. However, only few studies have been interested in mixed precipitation phenomenon, due mainly to its complexity (Sheikholeslami and Sudmalis 2000; Sheikholeslami 2003; Zarga et al. 2013). Indeed, the study of the interactive effect of salts in mixed precipitation with or without common ions is not widely discussed. Solubility effect, ionic strength, crystal structure and inhibitory effect are still not well defined in the co-precipitation process.

Studies that have been interested on CaCO_3 and gypsum mixed precipitation (MacAdam and Parsons 2004) using temperature-

controlled batch tests showed that the co-precipitation germination time and kinetics follow that of pure CaCO_3 , while the thermodynamic calcium concentrations on co-precipitation follow that of pure gypsum. In addition, the structure of precipitates, compared with that observed by simple precipitation is influenced by the coexistence of the two salts.

Other studies have shown that in the case of mixed precipitation, three possibilities may occur: 1) the first salt can act as a foreign body and reduce the energetic barrier of the second precipitating salt, therefore, the germination time of the second compound is reduced (Sohnel and Mullin 1988; Zarga et al. 2013), 2) precipitates may have morphologies that are different from those obtained with the pure body formation reactions, and 3) the presence of a co-precipitation salt can affect the thermodynamic of the solution and subsequently influence the germination kinetic of other salts (Lu and Czanderna 1984; Sohnel and Mullin 1988).

This paper looks at qualitative analysis of gypsum and CaCO_3 simple and mixed precipitations from Kinetic and structural point of view. It also aims to find the appropriate method to follow the germination parameters of the two precipitating salts and to compare the simple and mixed precipitation kinetics.

1. Materials and methods

2.1 Double decomposition method and experimental unit

Solutions were prepared with double decomposition method using two solutions of sodium sulfate (Na_2SO_4), sodium bicarbonate (NaHCO_3) and calcium chloride (CaCl_2). This method is mainly used to reach high supersaturations. In contrast to the dynamic method for which supersaturation is gradually decreased up to precipitation, the double decomposition method allows only for a specified supersaturation to observe or not the precipitation (Elfil and Roques 2001).

Solutions may contain calcium, bicarbonate, sulfate, sodium and chloride ions in significant quantities. Na^+ and Cl^- ions are involved in the precipitation process by means of ionic strength which is adjusted by the addition of sodium chloride (Sohnel and Mullin 1988; Elfil and Roques 2001; Wu et al. 2010). A schematic of the experimental setup used in this investigation is presented in Figure 1.

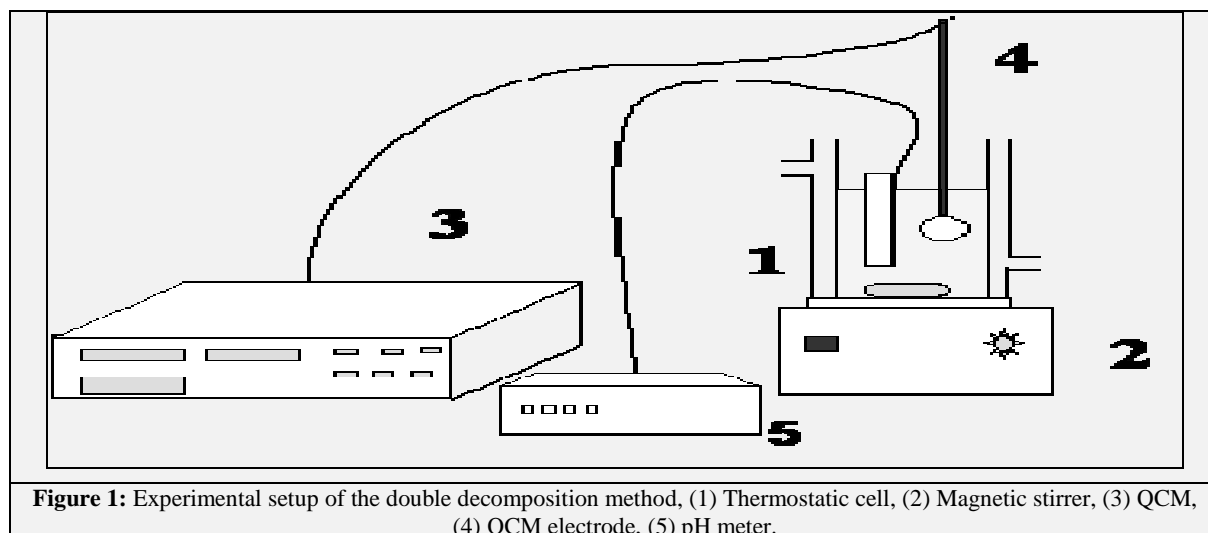


Figure 1: Experimental setup of the double decomposition method, (1) Thermostatic cell, (2) Magnetic stirrer, (3) QCM, (4) QCM electrode, (5) pH meter.

A thermostatic cell (1) of a capacity of 250 mL was used to maintain the solution at constant temperature by a thermostatic liquid circulation. The magnetic stirrer (2) was used to keep the solution homogeneous. The type of the used quartz crystal microbalance (QCM) was PM-720 Plating Monitor (3) equipped with a QCM electrode (4) that detect a very small mass (10^{-9} g) of precipitate deposited on its active surface. The solution pH was measured using Hanna Instrument HI 931401 pH meter (5).

2.2 Outgassing

This technique aims to separate the different kinetic steps in order to isolate the one which is required in the overall kinetics of the reaction (Marshall and Slusher 1966). This method corresponds generally to the material transfer to the solid/liquid interface. Furthermore, all the experiments have been performed under gaseous atmosphere to perfectly control the variations of dissolved CO_2 because its concentration is the main scaling system evolution driver. A schematic of the experimental setup of the degassing method is shown in Figure 2.

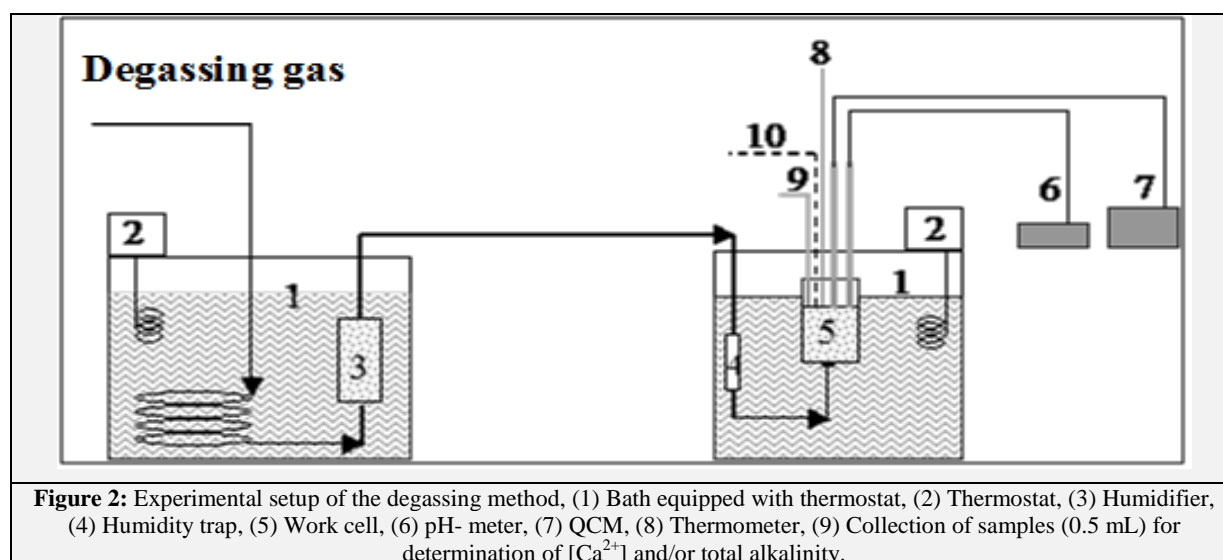


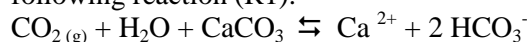
Figure 2: Experimental setup of the degassing method, (1) Bath equipped with thermostat, (2) Thermostat, (3) Humidifier, (4) Humidity trap, (5) Work cell, (6) pH- meter, (7) QCM, (8) Thermometer, (9) Collection of samples (0.5 mL) for determination of $[\text{Ca}^{2+}]$ and/or total alkalinity.

The solution was placed in the work cell (5), immersed in a thermostatic bath (1). The cell is provided at the lower part by a gas inlet at a perforated bottom which ensures its uniform

dispersion throughout the liquid. The gas flow rate is set at 6 L/min for all experiments. pH and $[\text{Ca}^{2+}]$ evolution are followed and monitored throughout the experiment.



Studied solutions are made by dissolving a known amount of CaCO_3 bubbling pure CO_2 in ultrapure deionized water. After paddling, the dissolution is completed according to the following reaction (R1):



2.3 Selection of parameters

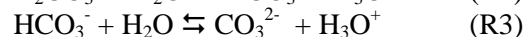
Experimental results of the kinetics of gypsum and CaCO_3 precipitations are relatively complex, especially in the case of mixed precipitation. Indeed, it requires accurate knowledge of the parameters at which a significant variation characterizes the germination of a precipitate or another. Throughout the experiments, measurements of several parameters were performed simultaneously.

To monitor CaCO_3 precipitation, pH, calcium concentration $[\text{Ca}^{2+}]$ and total alkalinity (TAC) are essential; QCM can also provide some clarifications.

Concerning the gypsum precipitation, its kinetic is followed with $[\text{Ca}^{2+}]$ variation; the QCM allows also the determination of its germination time accurately.

The study of the mixed precipitation kinetic is therefore performed by monitoring four parameters, namely: pH, $[\text{Ca}^{2+}]$, TAC and QCM response.

1) pH is essential to monitor CaCO_3 precipitation. Indeed, CaCO_3 germination is always accompanied by the release of hydronium ions responsible for a sudden drop in the solution pH. Precipitation of CaCO_3 is strongly dependent on the dissociation reactions (R2) and (R3):



The application of the mass action law to these two ionization reactions allows having the following relationships:

$$K_1 = \frac{(\text{HCO}_3^-)(\text{H}_3\text{O}^+)}{(\text{CO}_2)} \quad (1)$$

$$K_2 = \frac{(\text{CO}_3^{2-})(\text{H}_3\text{O}^+)}{(\text{HCO}_3^-)} \quad (2)$$

The combination of these equations is used to draw the percentages of the various carbonate species versus pH, as shown in Figure 3.

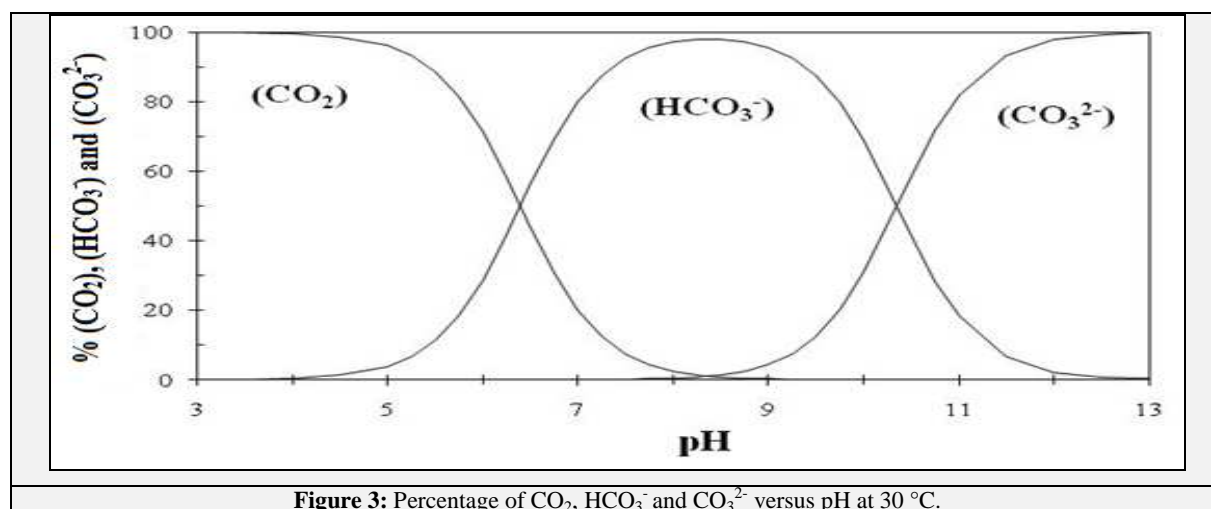


Figure 3: Percentage of CO_2 , HCO_3^- and CO_3^{2-} versus pH at 30 °C.

Figure 3 shows that:

For $\text{pH} < 5$ at 30 °C, the solution contains essentially of dissolved CO_2 . The solution is aggressive.

For $\text{pH} = \text{p}K_1$ (≈ 6.4 at 30 °C), we have a mixture of 50% CO_2 and 50% dissolved HCO_3^- ions.

For $\text{pH} = \frac{\text{p}K_1 + \text{p}K_2}{2}$ (≈ 8.3 at 30 °C), the solution consists essentially of HCO_3^- ions. From this pH value, the presence of carbonate ion (CO_3^{2-}) begins to be noticeable ($\approx 1\%$).

For $\text{pH} = \text{p}K_2$ (≈ 10.3 at 30 °C), the solution contains 50% HCO_3^- ions and 50% CO_3^{2-} ions.

Under normal operating conditions, the stock solution has a pH less than $\frac{\text{p}K_1 + \text{p}K_2}{2}$, the HCO_3^- ions predominate compared to CO_3^{2-} ions.

The determination of HCO_3^- ions, therefore, allows us to follow the CaCO_3 precipitation kinetic because it requires the consumption of bicarbonate ions and therefore a collapse of TAC.

2) Ca^{2+} contributes simultaneously to the precipitation of sulfate and CaCO_3 . Since the solubility of gypsum is much greater than that of CaCO_3 ($K_s(\text{gypsum})/K_s(\text{CaCO}_3) \approx 700$), the fraction of Ca^{2+} which corresponds to the gypsum germination will be very large compared to that corresponding to the CaCO_3 precipitation. So this parameter will be used to follow the gypsum precipitation kinetics.

3) QCM has often been used to measure very small changes in mass (about 10^{-9} g) deposited on its active face (Lu and Czanderna 1984). It uses the change of the resonance frequency of a quartz crystal which varies in proportion to the mass of foreign material deposited on its active face.

The QCM has been introduced in the field of CaCO_3 precipitation by Rosset et al., (Rosset 1984), developing Chrono Electrogravimetric technique (Khalil et al. 1992) based on the same principle as controlled potential chronoamperometry. Thereafter, in studying the scaling phenomenon by degassing

technique to atmospheric air, Roques (1995) has introduced the QCM as a complementary method to pH measurement and calcium dosage. QCM was also used to study the nature of CaCO_3 germination (Marshall and Slusher 1966) and the chemical inhibition of gypsum precipitation (Makhlouf 2000). In this work, QCM was used to determine the CaCO_3 and sulfate germination time.

3. Results and Discussion

3.1 CaCO_3 precipitation

For pure calco-carbonic solutions ($\text{Tca} = \text{TAC}$) with hardness ranging between 25 and 50 °f, the precipitation kinetics of CaCO_3 was monitored by the degassing method. $[\text{Ca}^{2+}]$ and pH evolution of the calco-carbonic solution (at 50 °f) degassed by atmospheric air is presented in Figure 4. CaCO_3 germination time was determined simultaneously from Tca and pH values. Indeed, Figure 4 shows that the start of CaCO_3 precipitation is identified by a drop in the pH accompanied by a decrease in $[\text{Ca}^{2+}]$.

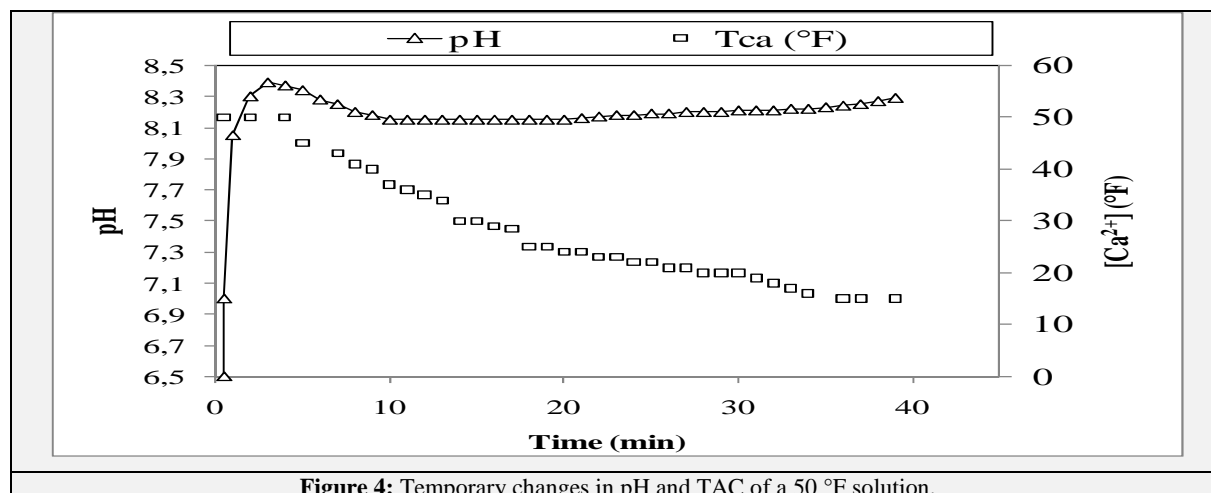
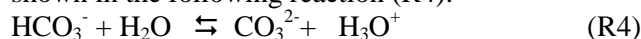


Figure 4: Temporary changes in pH and TAC of a 50 °F solution.

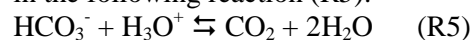
Indeed, a progressive degassing induces an increase in the pH of the solution to achieve a value of early precipitation. Early CaCO_3 germination is identified by a drop in pH, generally interpreted as follow:

Under normal operating conditions, pH of the solution is in its lower value of $\frac{pK_1 + pK_2}{2}$, HCO_3^- ions predominate in advance of CO_3^{2-} ions suggesting that the crystal growth occurs mainly between Ca^{2+} and HCO_3^- ions and not between Ca^{2+} and CO_3^{2-} ions. However, the transformation of HCO_3^- into CO_3^{2-} before it can be included in the crystal is necessary, as shown in the following reaction (R4):



The release of hydronium ions which is also necessary for stoichiometric reasons is responsible for the observed drop of pH.

Once the germination starts, the rate of release of hydrogen ions becomes important and the electronic neutrality is respected, as it is shown in the following reaction (R5):



In the solution, Ca^{2+} is associated with 2 HCO_3^- . However, in the crystal it is associated with a single CO_3^{2-} ion. It is therefore necessary to eliminate one carbon ion as seen in reaction (R5). It is the release of CO_2 that is responsible of immediately recovered PCO_2 balance. This leads to a CO_2 accumulation rate



that is greater than its elimination rate by degassing. The precipitation speed decreases thereafter, while the speed related to degassing gas flow remains constant. There is a moment

when the vent becomes faster than the accumulation of CO₂, while the pH of the solution increases. Results were reproduced for TCa of 25, 30, 40 and 50 °f (see Table 1).

Table 1: Summary of CaCO₃ germination parameters observed for various concentrations at 30 °C.

TCa _i (°f)	pH _G	T _G /TCa (min)	T _G /pH (min)	Ω calcite	Ω CCM	PCO _{2G} (atm)
50	8,40	4	5	92,3	4,47	3.10 ⁻³
40	8,55	5	6	86,81	4,19	2.23.10 ⁻³
30	8,53	12	13	67,79	3,27	1.21.10 ⁻³
25	8,54	14	14	41,77	2,02	9.74.10 ⁻⁴

CaCO₃ germination time is inversely proportional to the initial [Ca²⁺] of the solution. That is to say, the higher the TCa, the higher is the supersaturation and the faster is the germination. In some cases, T_G obtained by the pH meter response is slightly longer than that of the precipitation. This can be explained by the fact that at the beginning of germination, the precipitation rate is not high enough. Therefore, the release of CO₂ by degassing when the first germs appear is more significant than the amount of CO₂ contributing to the reaction.

3.2 Gypsum precipitation

Figure 5 shows the [Ca²⁺] evolution and the QCM response during calcium sulfate precipitation obtained by the double decomposition method. It is noticed that the beginning of precipitation (T_G) was detected by both QCM and Ca²⁺ ion concentration.

At the germination time, which is observed by the beginning of the TCa decrease, some gypsum germs are deposited on the active surface of the QCM electrode whose response has been instantaneous.

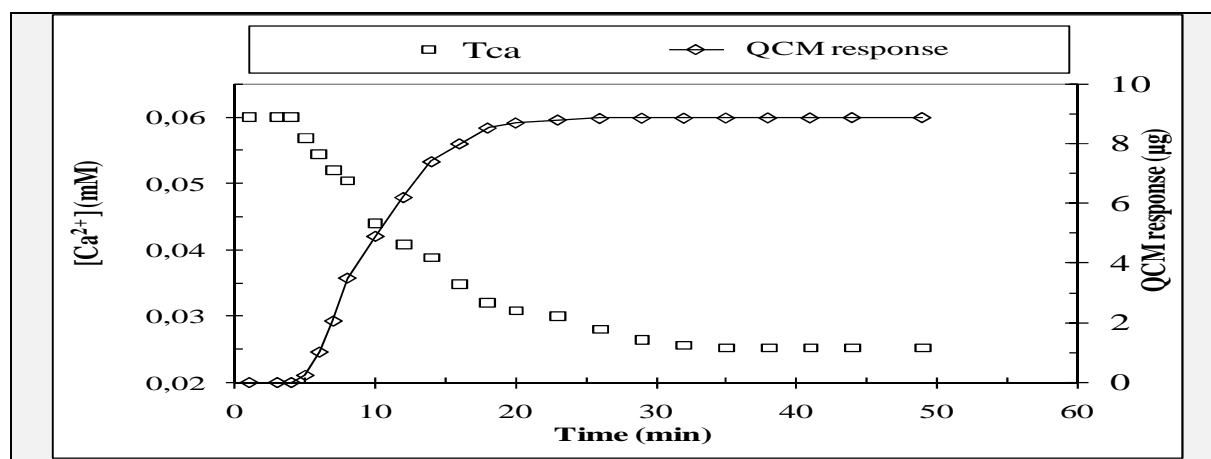


Figure 5: Evolution of [Ca²⁺] and QCM response during gypsum precipitation by the double decomposition method at 30°C.

We can, therefore, conclude that the QCM response and the monitoring of [Ca²⁺] are the most appropriate parameters to detect the gypsum germination time. Table 2 summarizes the results of [Ca²⁺] values ranging between 40 and 80 mM. It is clear that the germination time, determined by both QCM response and the drop of [Ca²⁺], decreases with increasing

the initial concentration of calcium sulfate solution, and therefore with the increase of the supersaturation with respect to gypsum. Indeed, T_G decreases from 44 to 1 minute when varying from an initial supersaturation of 3.1 to 6.7. Thus, supersaturation of the solution with respect to gypsum represents the driving force of the precipitation process.



Table 2: Gypsum germination time versus initial $[Ca^{2+}]$ at 30 °C.

TCa_i (mM)	T_G (min)	Ω (initial)	Ω (end of the experiment)
80	1	6,7	1,1
70	2	6,6	1,1
60	4	5,3	1,2
50	10	4,1	1,2
40	44	3,1	1,6

Supersaturation values corresponding to the end of experiments vary between 1,1 and 1,2. In other words, at the end of the experiments the ion activity product of the solution is almost equal to the gypsum solubility product limit. Depending on the time required to reach equilibrium (stabilization of calcium as an indicator of gypsum precipitation limits) it is clear that the nucleation process and the crystal growth become faster at higher supersaturation.

The study of gypsum precipitation by the double decomposition method shows that the QCM response as well as monitoring $[Ca^{2+}]$ is the most appropriate method to detect the exact time of the start of gypsum germination.

3.3 Co-precipitation

Gypsum and $CaCO_3$ mixed precipitation Kinetics have been studied by the double

decomposition method and by following four parameters, mainly: TCa , total alkalinity, pH and QCM response.

For a solution of initial concentrations $[Ca^{2+}] = 63$ mM, $[SO_4^{2-}] = 60$ mM, and total alkalinity = 30 °f, the precipitation of $CaCO_3$ is followed by the evolution of total alkalinity and pH, whereas gypsum germination is observed by a decrease in the calcium ion concentration which is a common ion of the tow (seed) precipitates. In fact, pH is an important parameter to monitor $CaCO_3$ germination in the co-precipitation process since gypsum germination is independent of this parameter (Zarga et al. 2013).

Figure 6 illustrates the important role of pH evolution which is followed by the drop of the bicarbonate ion concentration.

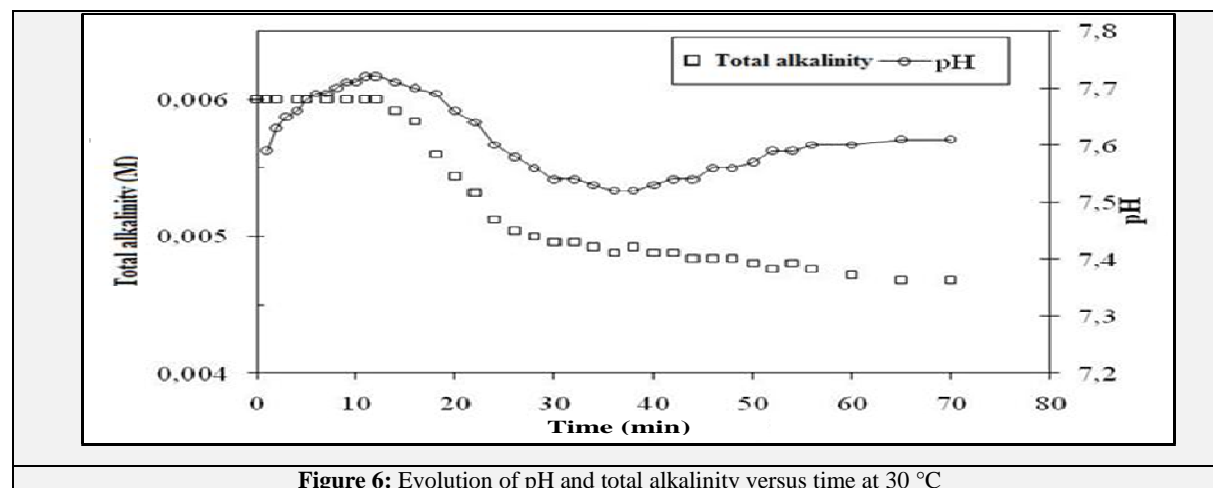


Figure 6: Evolution of pH and total alkalinity versus time at 30 °C

The evolution of $[Ca^{2+}]$ is virtually identical to that obtained in the simple precipitation kinetics; the only difference is the gypsum germination time which varies from 4 minutes in the case of simple precipitation to 9 minutes in mixed precipitation.

The variation of germination time is confirmed by Figure 7, which shows the evolution of the mass of the precipitate and the concentration of sulfate, and by the results presented in Table 3.

Table 3: Germination time of the tow precipitates detected by various parameters.

T _G (min)	Total alkalinity decrease	pH drop	[SO ₄ ²⁻] decrease	QCM response
	Relative to CaCO ₃ germination		Relative to gypsum germination	
	12	12	9	9

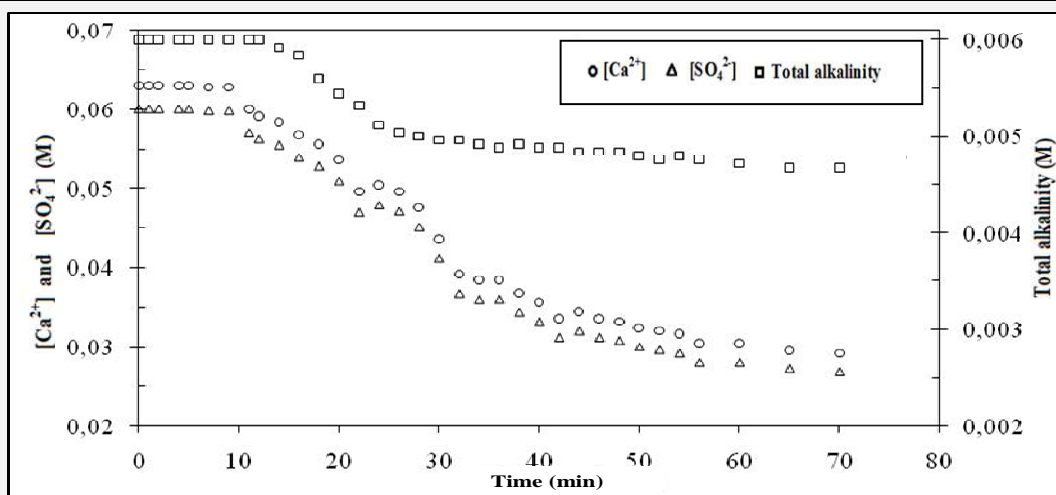


Figure 7: Evolution of calcium and sulfate concentrations and total alkalinity versus time at 30 °C ([Ca²⁺] = 63 Mm, [SO₄²⁻] = 60 Mm, total alkalinity = 30 °f).

It was observed that the gypsum germination began with a considerable drop in [Ca²⁺] accompanied by a significant change in the

QCM response, as shown in Figure 8 and Table 3. This is valid even when these changes are not followed by an alkalinity or a pH drop.

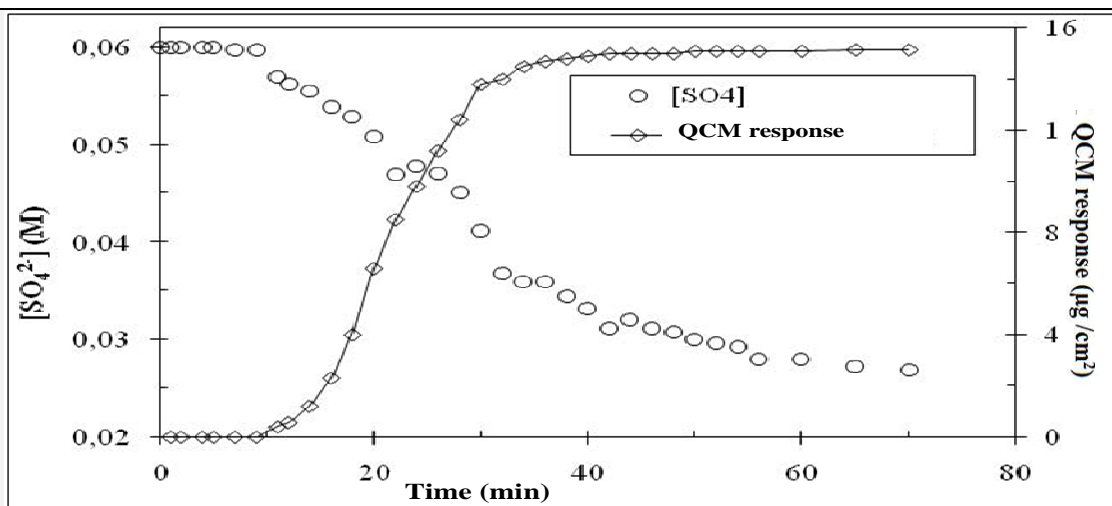


Figure 8: Evolution of [SO₄²⁻] and QCM response at 30 °C.

We can say in this case that the QCM response is specific to the gypsum germination because it is the salt which precipitates first. In this case, the QCM does not provide any

information on the CaCO₃ germination because even after the apparition of the first CaCO₃ germs, gypsum germination continues with a faster kinetic.



Table 4: CaCO₃ and gypsum germination times on “CaSO₄ - CaCO₃ - H₂O” and “CaSO₄ - H₂O” systems.

TCa _i (mM)	[SO ₄ ²⁻] (mM)	Mixed precipitation					Simple precipitation			
		T _G CaCO ₃ (min)			T _G CaSO ₄ (min)		T _G CaSO ₄ (min)			
		T _G / pH	T _G / TAC	Ω	T _G / QCM	T _G / SO ₄	Ω	T _G / QCM	T _G / SO ₄ ²⁻	Ω
83	80	3	4	1,52	1	1	3,28	1	1	3,2
73	70	5	5	1,21	4	4	2,82	2	2	2,77
63	60	12	13	1,83	9	9	2,37	4	4	1,86
53	50	18	19	2,29	26	28	1,91	10	10	1,41

Table 4 summarizes the CaCO₃ and gypsum germination times for various experiments of co-precipitation. It is noticeable that for solutions with high concentrations of sulfate and calcium ions ($\geq 0,06$ M), gypsum precipitates before CaCO₃. In this case, the QCM response is in good agreement with the specific volumetric assays related to gypsum germination. On the other hand, for low concentrations ($\leq 0,05$) CaCO₃ precipitates before the gypsum and confusion begins to appear between germination times detected by the QCM response and volumetric dosing. In this case, the QCM can detect the CaCO₃ seeds that appear before the gypsum crystals, hence the imprecision of the QCM response.

The germination time of gypsum in the "CaSO₄-H₂O" and "CaSO₄-CaCO₃-H₂O" systems is also presented in Table 4. The germination time for gypsum co-precipitation is higher than that corresponding to the simple precipitation ("CaSO₄-H₂O" system). This could be explained by the presence of electrostatic interactions between Ca²⁺, HCO₃⁻ and CO₃²⁻, on one hand, and between Ca²⁺ and SO₄²⁻ in "CaSO₄-CaCO₃-H₂O" system, on the

other hand. In other words, it is explained by the competition between SO₄²⁻, HCO₃⁻ and CO₃²⁻ ions.

Figure 9 represents the ion activity product of CaCO₃ versus time for different initial concentrations of sulfate. These results support the interactive effect between SO₄²⁻, HCO₃³⁻ and CO₃²⁻ ions. Indeed, for the same concentration of calcium, the induction time of CaCO₃ increases with the concentration of sulfate ions.

In the beginning of experiments, solutions used in this study were supersaturated with respect to CaCO₃ monohydrate. This shows the important role of the hydrated forms in the germination process of CaCO₃ (Marshall and Slusher 1966). Indeed, the spontaneous nucleation can occur only if one of the hydrated forms, called precursor, appears. If the supersaturation state does not lead to the formation of one of these precursors, the system remains in a state of metastability. That means the supersaturation of calco-carbonic system over anhydrous forms is insufficient for spontaneous nucleation of CaCO₃.

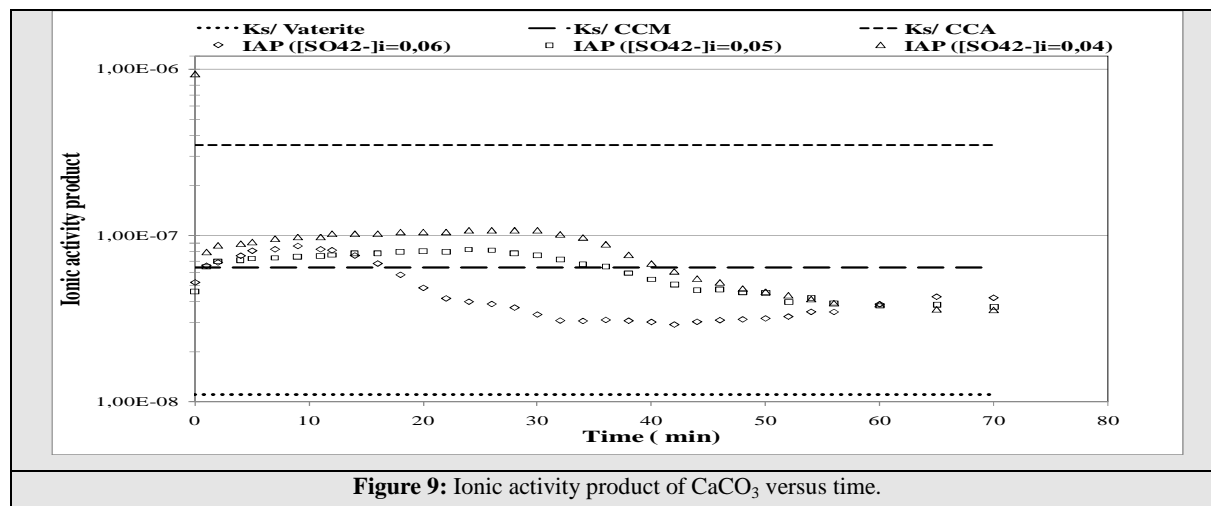


Figure 9: Ionic activity product of CaCO₃ versus time.



4. Conclusion

In this study, germination of gypsum and CaCO_3 was performed following four parameters simultaneously, namely: pH, the QCM response, and calcium and carbonate alkalinity concentrations. The germination time was difficult to monitor, especially for highly concentrated solutions. pH was found to be the key parameter for detecting CaCO_3 germination in a pure calco-carbonic system and in mixed precipitations. As for the response of QCM, it lacks precision for detecting CaCO_3 germination when it precipitates after gypsum. Comparing the germination time obtained in the co-precipitation case with those determined during the precipitation of one salt, it was found that the kinetics of the precipitation of gypsum become slower in presence of carbonates. Bicarbonates that interact with calcium ions have an important effect on delaying gypsum precipitation. In contrast, the presence of gypsum crystals can play a significant role in the nucleation of CaCO_3 . The method of double decomposition was proven to be very useful in studying calcium sulfate and CaCO_3 mixed precipitations. However, this method is very sensitive and requires high precision during the entire experimental protocol as there are multiple sources for error (e.g., calibration of the pH meter, preparation of solutions, dosages, reactor cleaning/wash, and development of the QCM).

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