SEMI-BATCH PRECIPITATION OF CALCIUM SULFATE DIHYDRATE FROM CALCITE AND SULFURIC ACID

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Abstract: The present work focuses on the physical and chemical aspects of a semi-batch precipitation of gypsum by injecting a calcite suspension to a sulfuric acid solution from industrial waste. The morphology of the precipitated crystals evolves from a needle-like shape to a platelet-like shape when temperature is increased from 25 to 90°C; when the initial concentration of the acid is increased from 15 to 30 wt%; or when the inlet flow of the suspension of calcite is decreased from 20 down to 5ml/min. The mean particle size increases from about 15 μm to about when temperature is increased from 25 to 90 °C and to about 160 μm when the inlet flows is decreased to 5 ml/min. A decrease in the speed of the propeller below 400 rpm is to be avoided as it induces the apparition of an undesired small sized crystal population to the detriment of the desired big sized crystal population. Apparent density of synthesized powders is affected by none of the parameters investigated but the inlet flow of the suspension which, being decreased from 20 to 5 ml/min, leads to an increase in the apparent density from 0.3 to 0.5. For each experiment, pH in water solution is about 8. Investigations are conducted on the influence of three calcite batches: two high purity calcites A1 and A2 from Urgonien limestone and a calcite B from Corbières limestone with high magnesium content. The presence of magnesium is suspected to lower the crystal size by inhibiting crystal growth, as mean particle size and apparent density are found to be smaller with a magnesium-rich calcite than with a high-purity calcite. Seeding experiments were conducted but did not show any enhancement in the mean particle size and in the apparent density.

Keywords: calcite, reactivity, semi-batch, experiment, gypsum, sulfuric acid, industrial waste.

1. INTRODUCTION

Gypsum is a mineral compound of first importance in the formulation of a wide range of building materials. To make up for the long term depletion of its natural resources, building material industry head more and more toward gypsum by-produced in other industrial sectors. Today, among such products, some are already added in different percentages to natural gypsum (phosphogypsum, desulfogypsum and titan-gypsum for example). Though, some other are still studied, especially gypsum produced by neutralizing sulfuric acid with lime. That neutralization process is frequently encountered in mining, metal or dye industries.

Nevertheless, if a lot of papers about gypsum crystallization thermodynamics and kinetics have been edited since the last decades (among them Marshall & Slusher, 1966; Witkamp et al., 1990; Freyer & Voigt, 2003), very few contributions can be found in literature on the topic of calcium sulfate

dihydrate precipitation from sulfuric acid taken as industrial wastewater and containing electrolytes at different valences (Singh & Garg, 2000; Gominšek et al., 2005). The aim of the present work (Bard, 2006; Bard & Bilal, 2010) is to lay the basis of a process for the production of synthetic gypsum valuable in plaster industry, and precipitated from sulfuric acid and limestone instead of lime to lower production costs. We investigated the influence of operating parameters, the particle size distribution of the calcite and the influence of its composition.

2. EXPERIMENTAL STUDY

For each semi-batch experiment, a 20 wt% (250g.l^{-1}) calcite suspension is injected in a 2l jacked reactor initially containing a sulfuric acid solution at desired concentration. A liquid organic compound, stable in the temperature range of this study, is used for thermal regulation by flowing through the reactor's jacket with the assistance of a

heating/cooling circulator bath. The calcite suspension is injected with a programmable peristaltic pump set at the desired inlet flow. When neutralization of the acid is almost reached, the resulting slurry is removed from the reactor and filtered. The liquid phase is stocked in a dedicated acidic waste tank, while the solid phase is washed with tap water (1l for 100g of solid) and dried at 50°C for at least 24h.

When dried, solid samples are broken up with caution in a mortar and finally analyzed. Their purity is controlled by FT-Infrared spectrometry and X-ray diffraction. Their shape is studied by scanning electron microscopy and their mean particle size determined by laser diffraction in wet medium. The apparent density of the powder samples is measured by the so-called «loose density» method, which consists in measuring the mass of a known volume of powder poured in a drum without cramming the solid into. This operation is accomplished in a 500 ml glass drum with a glass funnel to pour the powder through and a glass stick to level it. The pH of a slurry made of water and solid in a ratio of 20 ml of pure water for 1g of gypsum is measured after 15min mixing with a combined pH probe.

3. RESULTS

3.1 Influence of temperature and acid concentration

We have been studied crossed effects of temperature (25, 70, 80 and 90 °C) and acid concentration (15, 20 and 30 wt%). FTIR spectrometry and XRD confirmed that only gypsum has been precipitated. From SEM (Fig. 1, 2, 3) images, we observed that increasing the temperature at constant initial acid concentration leads to an evolution of the crystal shape from an acicular (i.e. needle-like) to a tabular (i.e. platelet-like) type.

Table 1. pH after 15min of aqueous suspensions of gypsum particles produced at different temperature from a 20 wt % calcite suspension and sulfuric acid at different initial concentrations.

H_2SO_4 content (wt%)	Temperature (°C)			
	25	70	80	90
15	8,0	8,3	8,1	8,4
20	8,1	8,4	8,2	8,3
30	8,3	8,3	8,1	7,8

In the meantime, at constant temperature, an increase in initial acid concentration seems to result in decreasing the length/width ratio of synthesized crystals. For each solid sample 5 g of washed and dried gypsum has been introduced in 100 ml of pure water and kept 15 minutes in suspension. Measured pH is around a value of 8 for all solid samples (Table 1).
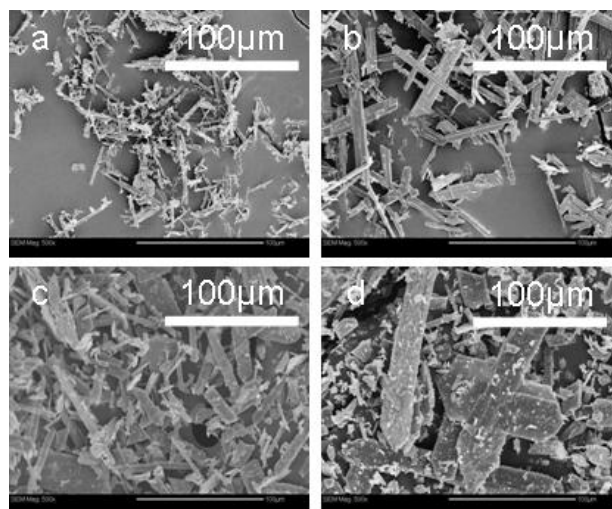

Figure 1. SEM images of gypsum crystals synthesized from a 20 wt% calcite suspension and 15 wt% initial acid concentration at: (a) 25 °C, (b) 70 °C, (c) 80 °C and (d) 90 °C.

Table 2. Mean particle size of gypsum crystals precipitated at different temperature from a 20 wt% calcite suspension and sulfuric acid at different initial concentrations.

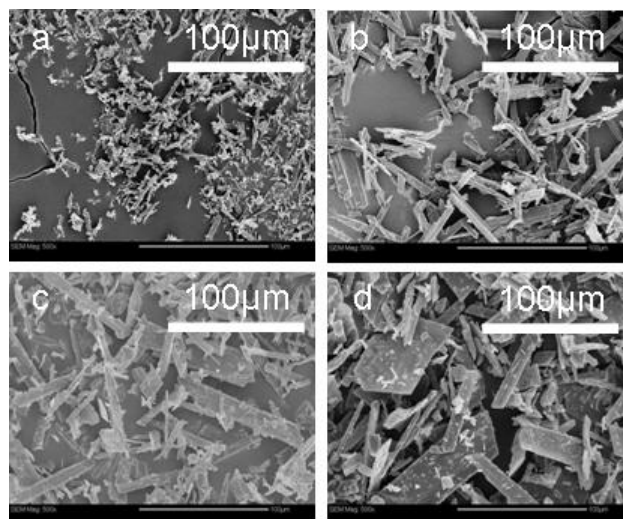| H_2SO_4 content (wt%)	Temperature (°C)			
	25	70	80	90
15	15μm	34μm	45μm	63μm
20	12μm	35μm	49μm	58μm
30	14μm	33μm	42μm	50μm

Figure 2. SEM images of gypsum crystals synthesized from a 20wt% calcite suspension and 20wt% initial acid concentration at: (a) 25°C, (b) 70°C, (c) 80°C and (d) 90°C.
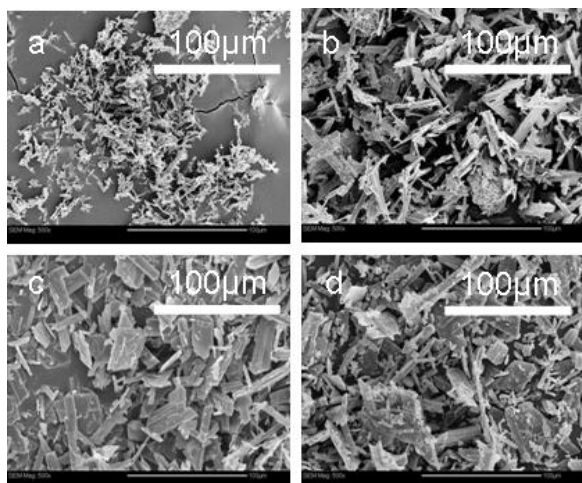
Figure 3. SEM images of gypsum crystals synthesized from a 20 wt% calcite suspension and 30 wt% initial acid concentration at: (a) 25 °C, (b) 70 °C, (c) 80 °C and (d) 90 °C.

Table 3. Apparent density of gypsum samples produced at different temperature from a 20 wt% calcite suspension and sulfuric acid at different initial concentrations.

H_2SO_4 content (wt%)	Temperature (°C)			
	25	70	80	90
15	0,275	0,280	0,285	0,280
20	0,280	0,285	0,280	0,285
30	0,275	0,280	0,280	0,280

From laser diffraction sizing (Table 2), the mean particle size (d_{50}) of the formed solid has been found to increase with the temperature at constant initial acid concentration. On the other hand, the effect of the initial acid concentration at constant temperature is to be neglected. We can also assume that the temperature has the major effect on morphology and size of the precipitated crystals.

We suppose that this constancy despite differences in process parameters setting resides in the fact that all samples have been plentifully washed after filtration. All powder samples present an apparent density of about 0.28 (Table 3). We can also assume that initial acid concentration and temperature have no influence on this powder's characteristic.

3.2 Influence of the agitation of the reacting medium

The effect of the propeller's rotation speed ω (in rpm) generating the medium's agitation has been studied at 90 °C. It has been found to have neither influence on the crystals' shape and size (Fig. 4) nor on powder's apparent density (Table 4).

Table 4. Apparent density of gypsum samples synthesized at 90°C with various propeller's radial speed from a 20wt% calcite suspension and sulfuric acid at various initial concentrations.

Initial acid concentration (wt %)	Propeller's radial speed ω (rpm)	
	200	400
15	0,280	0,285
20	0,280	0,280
30	0,285	0,280

As turbulence decreases appears a new population of smaller particles to the detriment of the former one (Fig. 5). We noticed that the lower the acid's initial concentration, the stronger this phenomenon. This could possibly explain the increasing discrepancy between the mean particle sizes of the two populations as initial acid concentration decreases (Table 5).

Table 5. Mean particle size (μm) of gypsum crystals precipitated at 90°C with various propeller's radial speed from a 20wt% calcite suspension and sulfuric acid at various initial concentrations.

Initial acid concentration (wt %)	Propeller's radial speed ω (rpm)	
	200	400
15	36	45
20	35	49
30	40	42

3.3 Influence of the inlet flow of calcite suspension

Influence of the inlet flow of the 20 wt% calcite suspension has been studied at 90 °C with an initial acid concentration of 15 wt% and a propeller's radial speed of 400 rpm. We observed a decrease in the length/width ratio while decreasing the inlet flow from 20 ml/min down to 5 ml/min (Fig. 6). We also noticed an increase in the contrast between the particle populations located at about 20 μm and 100 μm, coupled with an increase in the mean particle size as the inlet flow of the calcite suspension decreases (Fig. 7 and Table 6). We also observed that the mean particle size of the precipitated gypsum increases as the inlet flow decreases.

We supposed that this increase in particle size is linked to the evolution of supersaturation.
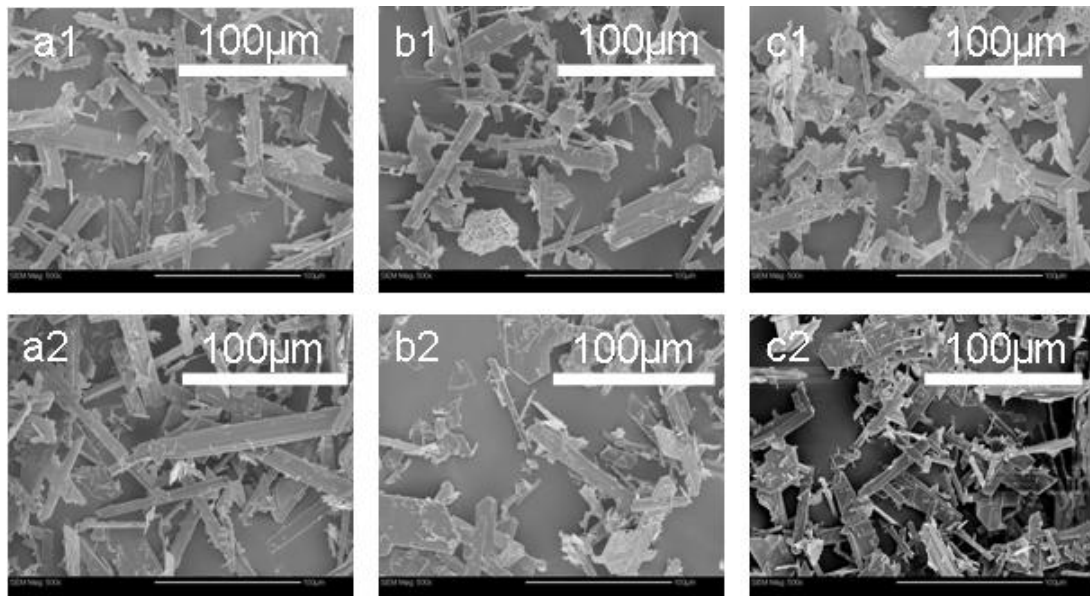
Figure 4. SEM images of gypsum crystals synthesized from a 20wt% calcite suspension and sulfuric acid: (a1) 15 wt% - ω = 200 rpm; (a2) 15 wt% - ω = 400 rpm; (b1) 20 wt% - ω = 200 rpm; (b2) 20 wt% - ω = 400 rpm; (c1) 30 wt% - ω = 200 rpm; (c2) 30 wt% - ω = 400 rpm.
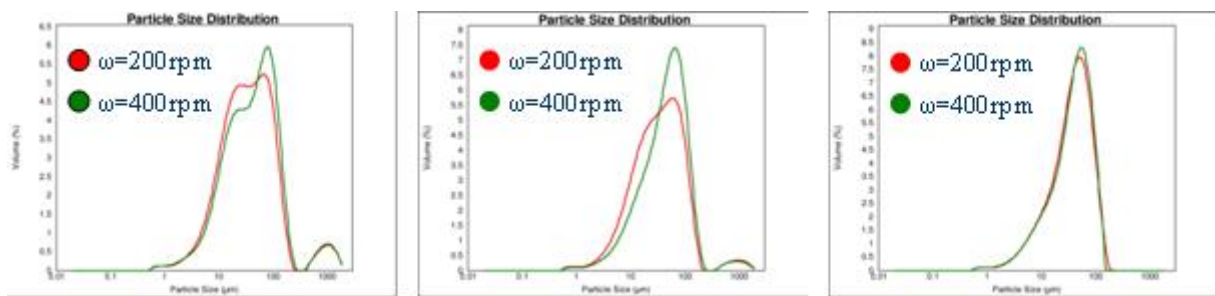

Figure 5. particle size distributions of gypsum samples synthesized at 90 °C and 200 rpm (red line) and 400 rpm (green line) from a 20 wt% calcite suspension and sulfuric acid at the initial concentration of: (a) 15 wt%, (b) 20 wt% and (c) 30 wt%.

Indeed, the slower calcium is added to the reacting medium trough the dissolution of injected calcite suspension, the lower the maximum supersaturation will be. Since a high supersaturation favors a high nucleation rate (that is to say the production of numerous but small crystals) we assume that decreasing the inlet flow of calcite suspension leads to the generation of a weaker supersaturation and then to the production of less numerous but bigger crystals.

As the inlet flow of calcite suspension decreases, the apparent density of the gypsum's powder increases (Table 7). We assumed that such an increase in the apparent density is not resulting from the evolution of particles' shape and size. In this case it would have been observed while studying the influence of temperature and initial acid concentration where modifications of crystal shape and sizes had already been observed.
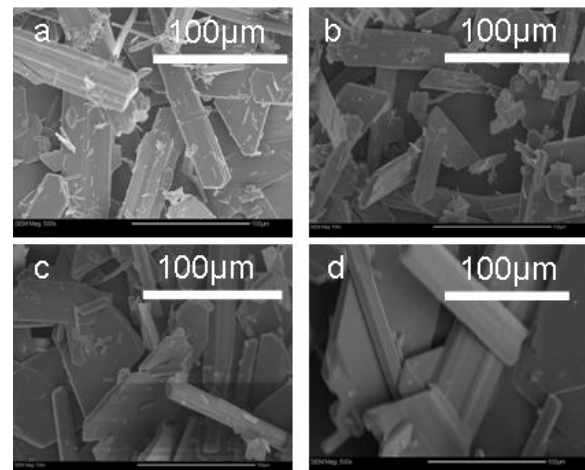

Figure 6. SEM images of gypsum crystals synthesized at 90 °C with a propeller's radial speed of 400 rpm from sulfuric acid 15 wt% and a 20 wt% calcite suspension injected with an inlet flow of: (a) 20 ml/min, (b) 15 ml/min, (c) 10 ml/min and (d) 5 ml/min.
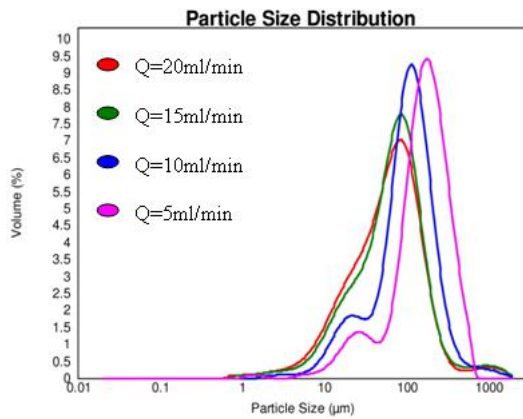
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Figure 7. particle size distributions of gypsum crystals synthesized at 90 °C with a propeller's radial speed of 400 rpm from sulfuric acid 15 wt% and a 20wt% calcite suspension injected at various inlet flows.

Table 6. mean particle size of gypsum crystals synthesized at 90 °C with a propeller's radial speed of 400 rpm from sulfuric acid 15 wt% and a 20 wt% calcite suspension at various inlet flows.

Calcite suspension inlet flow (ml/min)			
20	**15**	**10**	**5**
63μm	70μm	105μm	166μm

Table 7. apparent density of gypsum samples synthesized at 90 °C with a propeller's radial speed of 400rpm from sulfuric acid 15 wt% and a 20 wt% calcite suspension at various inlet flows.

Calcite suspension's inlet flow (ml/min)			
20	**15**	**10**	**5**
0,280	0,285	0,400	0,470

We better assumed that an increasing contrast between two well-defined populations of gypsum crystals combined with a tabular type results in a more compact stacking of the bigger particles in which the smaller can be stored easier.

3.3 Influence of calcite composition

On one hand, calcites from an Urgonien limestone and from Corbières limestone have different compositions in terms of major elements. More particularly The Corbières limestone contains the Mg element at a higher ratio (Table 8). On the other hand the two calcites have approximately the same mean particle size, that is to say 30 μm and 25 μm for calcites from the Urgonien and from the Corbières limestone respectively.

Two sets of experiments, conducted at 90°C with an initial sulfuric acid concentration of 15wt% in a reacting medium agitated at 400rpm, have been run. In the first set we decreased the inlet flow of suspension from 20 down to 5ml/min using the calcite A. In the second set, we used the same protocol, but with calcite B.

Table 8. Chemical compositions of calcites from Urgonien limestone (A) and Corbières limestone (B) are determined by X-ray fluorescence. LOI*: Loss On Ignition.

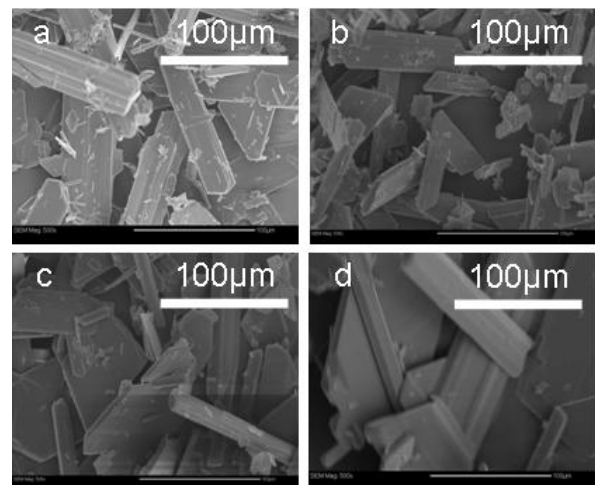| Elements wt%	**A**	**B**
SiO_2	0.02	0.02
TiO_2	0.01	0.01
Al_2O_3	0.01	0.02
Fe_2O_3	0.04	0.08
MgO	0.25	0.42
CaO	55.52	55.07
Na_2O	0.02	0.05
K_2O	0.04	0.09
P_2O_5	0.02	0.03
LOI*	42.90	41.42

Figure 8. SEM images of gypsum crystals synthesized at 90 °C from sulphuric acid 15 wt% and a 20 wt% suspension of calcite A injected with an inlet flow of : (a) 20 ml/min, (b) 15 ml/min, (c) 10 ml/min and (d) 5 ml/min.

After figures 8 and 9, we observed no differences between the two calcites in terms of influence on the morphological evolution of gypsum crystals while decreasing the inlet flow of the suspension. The calcite composition seems not to play any role with regards to the morphological behavior of the product. As the inlet flow decreases, we observed an increase in the mean particle size for both of the calcite, though the increase in the mean particle size is weaker for the experiments conducted with calcite B (Table 9). The particle size distributions show a bimodal distribution for solids precipitated with both calcites but the size contrast between the two populations is weaker for calcite B (Fig. 10). Calcites A and B exhibit a different

reactivity while decreasing the inlet flow of the suspension. More precisely, the mean particle size and the apparent density (Table 10) increase more weakly when calcite B is used.
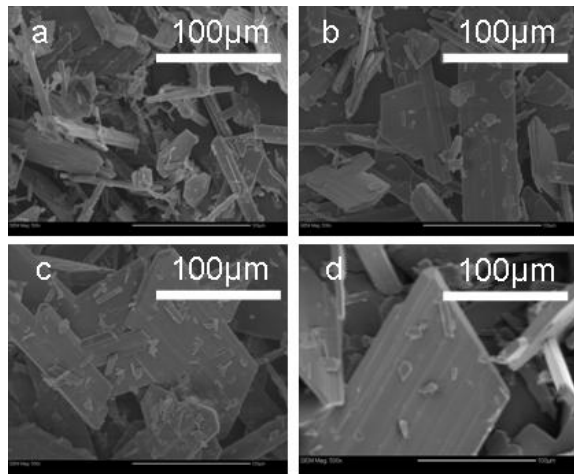

Figure 9. SEM images of gypsum crystals synthesized at 90 °C from sulphuric acid 15 wt% and a 20 wt% suspension of calcite B injected with an inlet flow of : (a) 20 ml/min, (b) 15 ml/min, (c) 10 ml/min and (d) 5ml/min.

Table 9. Mean particle size (µm) of gypsum crystals synthesized with calcites A and B suspensions injected at various inlet flows.

Calcite	Calcite suspension inlet flow (ml/min)			
	20	15	10	5
A	63	70	105	166
B	57	71	86	115

We may suppose that magnesium ions are responsible for such an inhibition of crystal growth as noticed earlier by Rashad et al. (2004). We then assume that the calcite A from Urgonien limestone should be use in preference to calcite B from Corbières limestone.

Table 10. Apparent densities of gypsum powders synthesized with calcites A and B injected at various inlet flows.

Calcite	Calcite suspension inlet flow (ml/min)			
	20	15	10	5
A	0,28	0,29	0,40	0,47
B	0,31	0,31	0,35	0,41

3.4. Influence of the calcite's particle size distribution

Calcite from Urgonien limestone has been separated in two batches. The first one has a mean particle size of 30µm (calcite A1) and the second one has a mean particle size of 60µm (calcite A2). Two sets of experiments, conducted at 90°C with initial sulfuric acid concentration of 15wt% in a reacting medium agitated at 400rpm, have been run. In the first set we decreased the inlet flow of suspension from 20 down to 5ml/min using the calcite A1. In the second set, we used the same protocol, but with calcite A2.

After figures 11 and 12, we observed no differences between the two particle sizes distributions in terms of influence on the morphological evolution of gypsum crystals while decreasing the inlet flow of the suspension. The calcite particle size distribution seems not to play any role with regards to the morphological behavior of the product.
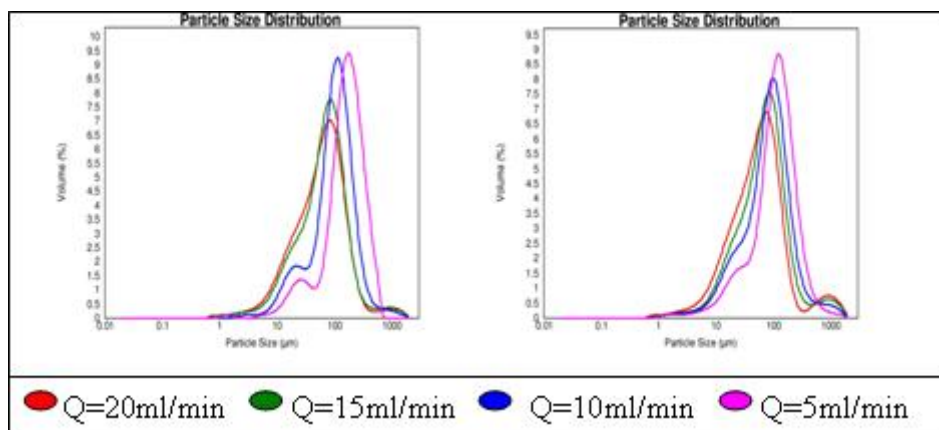

Figure 10. Particle size distributions of gypsum crystals synthesized at 90 °C from sulfuric acid 15 wt% and 20 wt% suspensions of calcite A (on the left) and calcite B (on the right) injected with Various inlet flows.
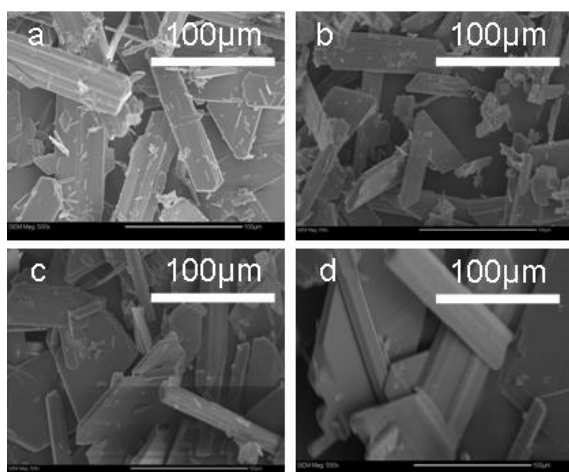
Figure 11. SEM images of gypsum crystals synthesized at 90 °C from sulfuric acid 15 wt% and a 20 wt% suspension of calcite A1 injected with an inlet flow of: (a) 20 ml/min, (b) 15 ml/min, (c) 10 ml/min and (d) 5ml/min.

As the inlet flow decreases, we observed an increase in the mean particle size for both of the calcites, though the increase in the mean particle size is stronger for the calcite A2 (Table 11). The particle size distributions appear to be bimodal for solids precipitated with both calcites but the size contrast between those populations seems stronger for calcite A2 (Fig. 13).

We may suppose that this behavior is due to the dissolution rate of calcite particles as already noticed by Hoşten and Gülsün (2004).

Table 11. Mean particle size (μm) of gypsum crystals synthesized with calcites A and C injected at various inlet flows.

Calcite	Calcite suspension inlet flow (ml/min)			
	20	15	10	5
A1	63	70	105	166
A2	74	91	124	183

Indeed, as the calcite particles of batch A2 are bigger than that of batch A, the reactive surface of batch A2 particles, is smaller than the reactive surface of batch A1 particles. As the dissolution rate of a solid is directly proportional to its reactive surface, particles from batch A2 dissolve more slowly than particles from batch A1, which implies that the supersaturation generated by these particles will be lower than if generated by the dissolution of the smaller particles from batch A1. Thus, a lower supersaturation will generate fewer crystals but of bigger size.

This may explain why the apparent density is slightly higher for gypsum powder precipitated from calcite A2 (which has a mean particle size of 60 μm) than for gypsum precipitated with calcite A1 (which has a mean particle size of 30 μm) (Table 11).

Calcites of different mean particle size have a different reactivity while decreasing the suspension inlet flow. More particularly, the mean particle size and the apparent density of the precipitated solid are higher when a calcite of higher mean particle size is used. It is also preferable to use a calcite with a higher mean particle size.

3.5. Seeding of the reacting medium with gypsum crystals

We studied the effect of seeding on calcite reactivity using the following set of parameters. A temperature of 90 °C, a sulfuric acid concentration of 15 wt%, an agitation speed of 400 rpm and a suspension inlet flow of 5 ml/min. We investigated this effect using 2 wt% and 10 wt% of tabular crystals of gypsum (Fig. 14).

Calcites A1 (Urgonien limestone – d_{50} = 30 μm), A2 (Urgonien limestone – d_{50} = 60 μm) and B (Corbières limestone – d_{50} = 25 μm) were used for each seed concentration.

We observed no evolution in the morphology of gypsum crystals synthesized with calcites A1, A2 and B while seeding the reacting medium with tabular gypsum crystals (Fig. 15-16).

Seeding with gypsum crystals induced a decrease in particle mean size of formed gypsum (Fig. 17 and Table 11). This effect is observed whatever the calcite used and the seed ratio. We may think that due to the high acidity of the reacting medium, gypsum seeds must have been dissolved very quickly and only contributed to enhance supersaturation which favored formation of many more and smaller crystals.

The decrease in mean particle size is accompanied with a decrease of the apparent density (Table 10).

4. DISCUSSION

Variation of temperature induces a variation of morphology and size of the precipitated gypsum. As temperature increases, the length/width ratio decreases resulting in an evolution of the crystal shape from an acicular (i.e. needle-like) type to a tabular (i.e. platelet-like) type. The mean particle size is affected by temperature too as it increases with this parameter.
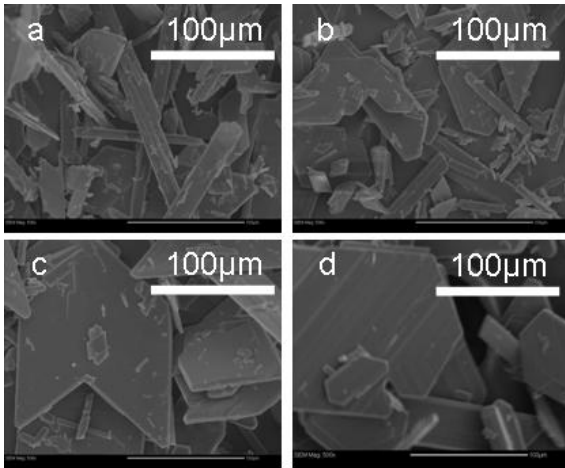
Figure 12. SEM images of gypsum crystals synthesized at 90 °C from sulphuric acid 15 wt% and a 20 wt% suspension of calcite A2 injected with an inlet flow of: (a) 20 ml/min, (b) 15 ml/min, (c) 10 ml/min and (d) 5ml/min.
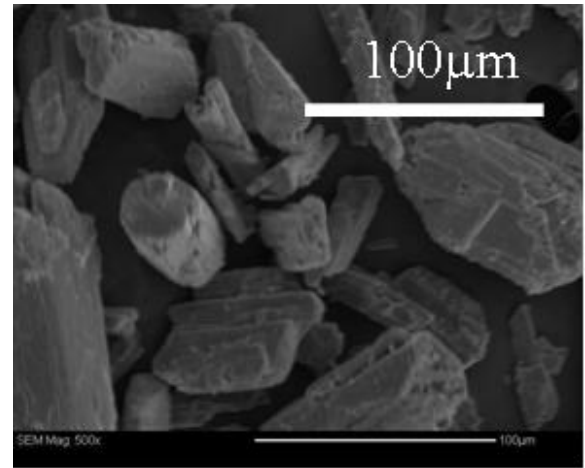

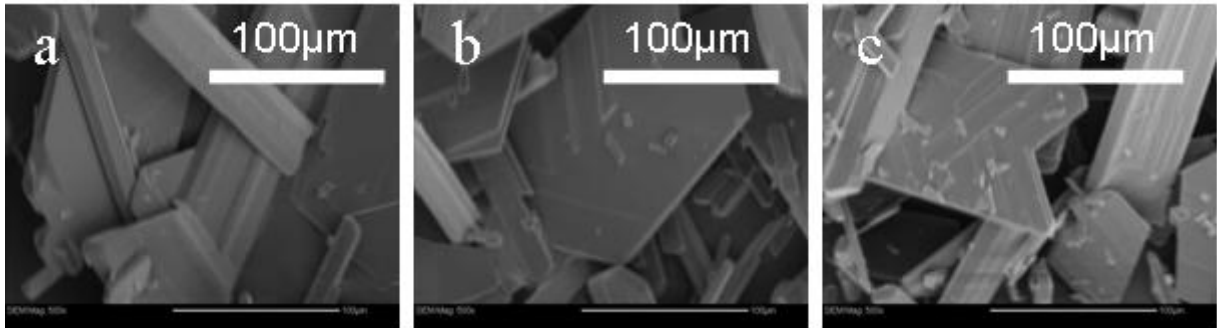Figure 13. SEM image of gypsum crystals used for seeding experiments.

Figure 14. SEM images of gypsum crystals synthesized from 20 wt% aqueous suspension of calcite A1 (a) without seeds, (b) with 2 wt% seeds, (c) with 10 wt% seeds.
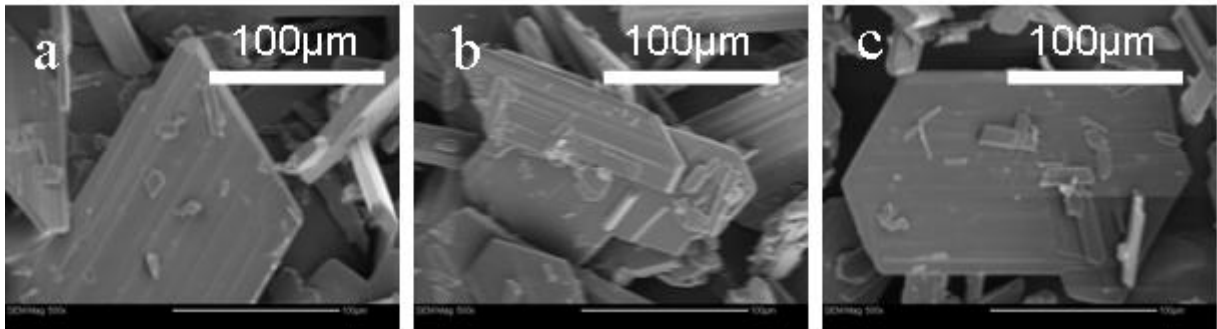

Figure 15. SEM images of gypsum crystals synthesized from 20 wt% aqueous suspension of calcite B (a) without seeds, (b) with 2 wt% seeds, (c) with 10 wt% seeds.
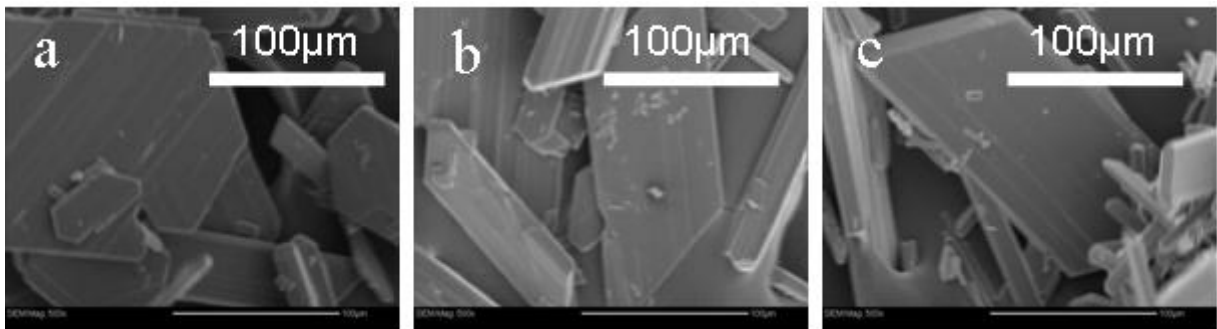

Figure 16. SEM images of gypsum crystals synthesized from 20 wt% aqueous suspension of calcite A2 (a) without seeds, (b) with 2 wt% seeds, (c) with 10 wt% seeds.
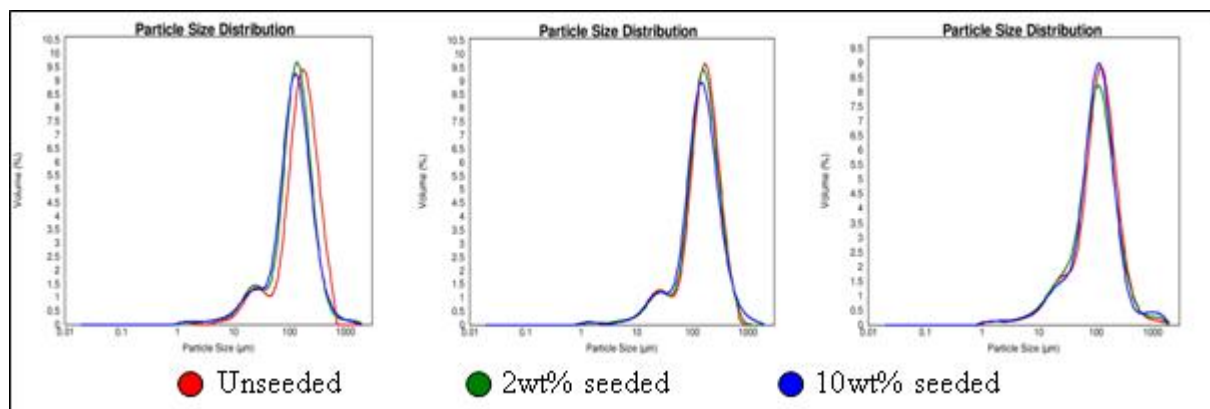
Figure 17. Particle size distributions of gypsum crystals synthesized from 20 wt% calcite A1 (left), A2 (center) and B (right) and suspensions in unseeded (red line), 2 wt% seeded (green line) and 10 wt% seeded (blue line) reacting medium.

An increase in the initial sulfuric acid concentration affects the morphology of produced crystals in the same way, but in contrary to the former parameter, that modification has no marked effect on the mean particle size of the gypsum powder. Both of these two process parameters have neither influence on the pH of the precipitated solid in water, nor on its apparent density.

Those results, more particularly the morphological evolution of crystals, lead us to focus on experiments conducted at 90 °C with an initial sulfuric acid concentration of 15 wt%, operating conditions for which crystals exhibit a shape the closer to those required by plaster industry.

The influence of the agitation of the reacting medium studied through the radial speed of the propeller has neither effect on the morphology nor on the pH and nor on the apparent density of the precipitated solid. Nevertheless, as this speed decreases a new population of smaller particles appears to the detriment of the initial bigger one. This phenomenon becomes more important as the initial sulfuric acid concentration decreases. We also assume that working with low agitation speed is to be avoided.

Variations of calcite suspension inlet flow leads to a variation of length/width ratio as well as a variation of mean particle size of produced crystals. More precisely, a decrease in suspension's inlet flow makes crystal shape evolve from acicular to tabular type and makes mean particle size increase significantly. The major evolution with regards to the product quality is certainly the improvement in its apparent density, which increases from 0.3 to 0.5 when decreasing the suspension's inlet flow from 20 down to 5 ml/min. We also assume that the lower the suspension's inlet flow; the better the quality of the precipitated gypsum.

5. CONCLUSION

The present work is focused on the physical and chemical aspects of the semi-batch precipitation of gypsum by injecting a calcite aqueous suspension to a sulfuric acid solution. The results help understand the impact of process parameters such as temperature, initial concentration of reactants (which actually represent the solid/liquid ratio of the reacting medium), and agitation of the reacting medium and the inlet flow of reactants.

The operating conditions are set so that the synthesis is conducted at 90 °C with an initial sulfuric acid concentration of 15 wt% (i.e. a solid/liquid ratio of about 13 %), with a propeller's radial speed of 400 rpm and an inlet flow of calcite suspension of 5 ml/min. These conditions lead to a good improvement of the product's apparent density, that is to say the better for valorization in plaster industry.

The temperature and the initial sulfuric acid concentration are chosen taking into account the most adequate length/width ratio for precipitated gypsum crystals. The radial speed of the propeller is chosen sufficiently high to keep a monomodal population size distribution with a mean particle size high enough to respect values expected by plaster industry, but not too high to avoid crystal breakage. The inlet flow of the calcite aqueous suspension is lowered as much as possible so that the supersaturation remains reasonable for the production of big tabular shaped gypsum crystals, but sufficiently high to avoid blocking of the inlet pipe by sedimentation of calcite particles.

From conducted investigations on the three calcite batches (from Urgonian limestone A1 and A2 and Corbieres limestone B) we established that, in order to produce a solid of best quality in terms of apparent density, it is preferable to use the calcite

from Urgonien limestone which is more pure with regards to the magnesium percentage than the Corbieres limestone. We also established that the bigger the particle size of dissolving calcite, the best the quality of the solid with regards to its apparent density. The seeding of the reacting medium failed in improving the latter characteristic of the produced powder. Not only the crystal shape does not evolve, but more the particle size and the apparent density decrease. Thus, introducing gypsum seeds directly in the reactor is not a good solution to improve gypsum powder's characteristics. We may suppose that the recycling of the gypsum sludge or the introduction of seeds at different time after the beginning of the crystal growth would have an interesting impact in terms of secondary nucleation.

6. ACKNOWLEDGEMENTS

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