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Morphological characteristics and aggregation of calcite crystals obtained by bubbling CO_2 through a $Ca(OH)_2$ suspension in the presence of additives

J. García-Carmona, J. Gómez-Morales*, J. Fraile-Sainz, R. Rodríguez-Clemente

Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Spain

Abstract

In this work, the authors studied the influence of citric acid, sucrose, calcium lignosulfonate, sodium dodecyl sulfate, polyethylene glycol and triethanolamine (1 wt.%) as well as of $CaSO_4 \cdot 1/2H_2O$ and aerosol OT (0.5 wt.%) on the morphology and aggregation of calcite precipitated by carbonation of slaked lime. It was found that the three first additives modify the precipitation mechanism yielding elongated agglomerates similar to those known as chain-like, precursors of colloidal nanometric calcite. The other additives used do not modify the mechanism and yield scalenohedral calcite of submicrometric/micrometric size, similar to that obtained in the absence of additives. These results are explained in terms of the effect of these additives on the dissolution rate of $Ca(OH)_2$ and their inhibitory effect in the chain-like to colloidal calcite transformation. Concerning the aggregation phenomena, sucrose and citric acid act aggregating the primary chain-like particles. Lignosulfonate aggregates on the whole size range. The other additives showed a small dispersing effect.
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Keywords: Chain-like calcite; Scalenohedral calcite; Additives; Conductivity monitoring; Aggregation

1. Introduction

Precipitated calcium carbonate (PCC) with given characteristics of morphology and crystal size distribution (CSD) is widely used as filler or pigment for rubber, plastics, paper, paints, etc. PCC is industrially obtained by the carbonation route, which consists of bubbling CO_2 gas through an aqueous suspension of slaked lime ($Ca(OH)_2$). Depending on the operating conditions, calcium carbonate crystallizes in different polymorphs including amorphous calcium carbonate (ACC), vaterite, aragonite and calcite [1–3]. Among them, calcite is the most important because of its greater stability at ambient temperature and its various morphologies, i.e. rhombohedral, scalenohedral, spherical, etc. The overall precipitation process of calcite involves steps such as nucleation, crystal growth and aggregation and/or breakage, all of them affecting the final CSD [4].

The calcium carbonate precipitation process by carbonation of slaked lime is a heterogeneous reaction ruled at nearly constant supersaturation. This is reflected generally in the constancy of the recorded values of pH and Ca^{2+} concentration as a function of time. After $Ca(OH)_2$ consumption, the supersaturation decreases until zero, indicating the end point of the neutralization [5–7]. However, it is difficult, by using a pH electrode, to detect slight concentration changes of OH^- ions in a solution with a high pH such as a suspension of lime. Yamada and Hara [5] showed that the measurement of the electrical conductivity (κ) is more sensitive than that of pH to monitor the concentration changes of dissolved species, i.e. Ca^{2+} and OH^-, or HCO_3^-, during carbonation because κ is nearly proportional to the concentration of dissolved $Ca(OH)_2$. These authors correlated the change of κ during the carbonation of lime with the changes in phase or morphology of the precipitates. They suggested the monitoring of κ as a method to follow these transformations.

Several factors including pH, supersaturation, temperature, type and concentration of impurities/additives, etc., play an important role in the crystal growth and aggregation phenomena. They affect the growth rates of the different crystal faces and the surface electrical properties of calcite during its growth in aqueous suspensions [8–12]. It was observed that the use of certain additives in small quantities (i.e. 1 wt.%) modify not only the sorptive capabilities of $Ca(OH)_2$ but also the morphological characteristics of the obtained PCC, depending on whether they are added during the

* Corresponding author. Tel.: +34-93-5801853; fax: +34-93-5805729.
E-mail address: jaime@icmab.es (J. Gómez-Morales).

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Table 1
Additives used in experiments of carbonation of slaked lime suspensions: 7.4 wt.% of $Ca(OH)_2$. Gas flow rate 7.5 dm^3/min, 35 °C

Chemical name	Abbreviation	Molecular formula	CAS number	Molecular weight
Citric acid	cit	$HOC(CH_2COOH)_2COOH$	77-92-9	192.12
Sucrose	sucrose	$C_{12}H_{22}O_{11}$	57-50-1	342.29
Calcium Lignosulfonate	ligno	$(-CH_2OH, -SO_3H$multiple$)$	8061-52-7	–
Sodium dodecyl sulfate	sds	$CH_3(CH_2)_{10}CH_2OSO_3Na$	151-21-3	288.38
Calcium sulfate hemihydrate	sulfate	$H_2O(CaSO_4)_2$	10034-76-1	290.29
Polyethylene glycol 300	petgl	$H(OCH_2-CH_2)_nOH$	25322-68-3	~ 300
Sodium dioctyl sulfosuccinate	aerosol OT	$C_{20}H_{37}O_4SO_3Na$	577-11-7	444.56
Triethanolamine	tie	$N(CH_2CH_2OH)_3$	102-71-6	149.19

slaking of the lime or directly during the carbonation process. Some commercial additives used for these purposes are citric acid, sodium dodecyl sulfate, sucrose, calcium lignosulfonate, polyethylene glycol 300, triethanolamine, sodium dioctyl sulfosuccinate and calcium sulfate hemihydrate [13–17]. Their influence on the growth, aggregation and crystal habit modification of industrial PCCs, however, has not been investigated from the point of view of the relationship between the structure of the additive and the mentioned properties. This study is of special interest to control the CSD and the shape of the crystals. With this work the authors pretend to analyze, on one hand, the relationship between the structure of these additives and the precipitation mechanism of industrial PCCs and, on the other hand, the magnitude of the aggregation or dispersion process produced by the same additives on the obtained products.

2. Experimental

The experimental set-up consisted of a double-wall Pyrex reactor of 2.2 dm^3 capacity provided of a vertical shaker, a thermostat, an INGOLD conductivity cell (cell constant $C = 1.01$), a pH electrode (ORION ROSS®), a conductivity meter, a pH-meter, a flow meter (Fischer and Porter) calibrated for 20% CO_2/80%N_2 (vv) and a computer that allows the continuous recording of the κ- and pH-signals.

The experiments were performed by bubbling a mixture of 20%CO_2/80%N_2 (vv) (Gas EAP 80 supplied by Carburos Metálicos) at a flow rate of 7.5 dm^3/min through 1.5 dm^3 of slaked lime suspensions of concentration 7.4 wt.% of $Ca(OH)_2$ (supplied by Cales de Llierca) and one of the above mentioned additives. The additives shown in Table 1 were added to the slaked lime suspensions after reaching a set point temperature inside the reactor of 35 °C. Their concentration, based upon the weight of $CaCO_3$ to be produced, was of 0.05 or 1 wt.%. The temperature of the experiment was maintained at 35 °C, in spite of the exothermic character of the reaction, by manipulating the temperature of the thermostat. The homogenization of the system was attained at stirring rates of 800 rpm. The whole precipitation process was followed by monitoring and recording the κ-signal continuously.

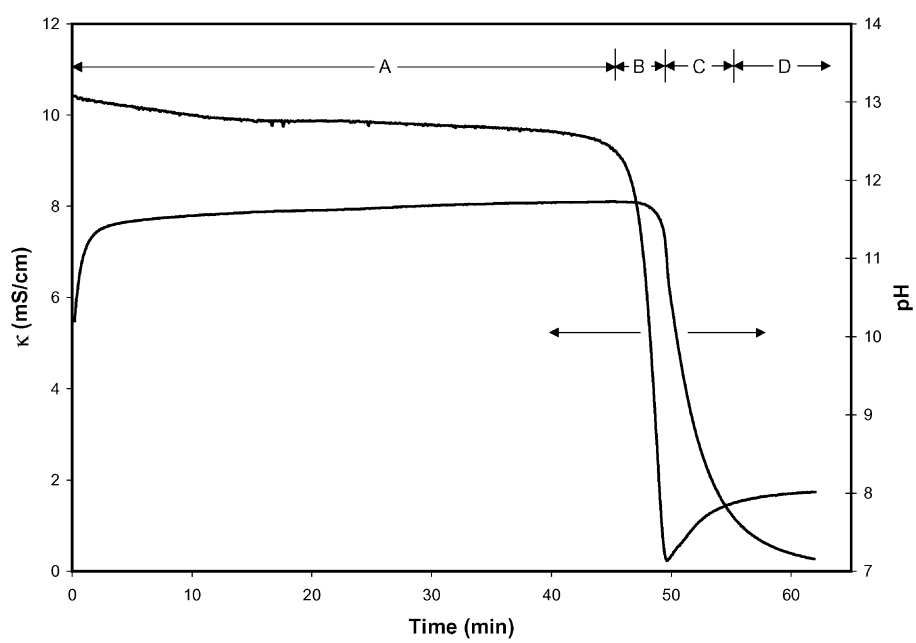

Fig. 1. Evolution of κ and pH during carbonation of 7.4 wt.% of lime at 35 °C.

Prior to this set of experiments, a blank experiment was performed without the use of any additive. This one was carried out in similar operating conditions than those performed in the presence of additives. In this case the pH was also recorded to compare the evolution of the κ- and pH-signals.

At the end of the experiments, an aliquot of the final suspensions was analyzed by the light scattering method, using a Coulter LS 130 instrument, to obtain the CSD. The rest of each suspension was filtered and washed with deionized water. The final white precipitate was dried in an oven with circulating forced air at 100 °C and weighed. Then, they were analyzed by X-ray diffraction (XRD) with a Rigaku Rotaflex RU200 B instrument, using $CuK\alpha_1$ (1.5405 Å) radiation and scanning electron microscopy (SEM) using a Hitachi S570 microscope. Finally, the specific surface area was measured by the Brunauer–Emmett–Teller (BET) method using an ASAP 2000 instrument (Micromeritics).

3. Results

3.1. Blank experiment

In Fig. 1, we appreciate clearly that the carbonation process can be followed by κ and pH monitoring. However, the end-point is marked by a more abrupt and quicker change in the κ-signal. This fact reveals that κ is more sensitive than pH to follow this process. The basic κ profile can be divided in four regions. In the initial one (A), the κ value is almost constant. In region (B), there is a large drop of the electrical conductivity followed by a slight increase in region (C). Finally, we observe a zone of stability where κ maintains a constant value in region (D). The minimum value of κ corresponds to the complete $Ca(OH)_2$ consumption. Beyond this point, the only solid present, confirmed by XRD, is calcite. SEM observation of the so obtained precipitate shows agglomerates of particles displaying scalenohedral habit (Fig. 2a).

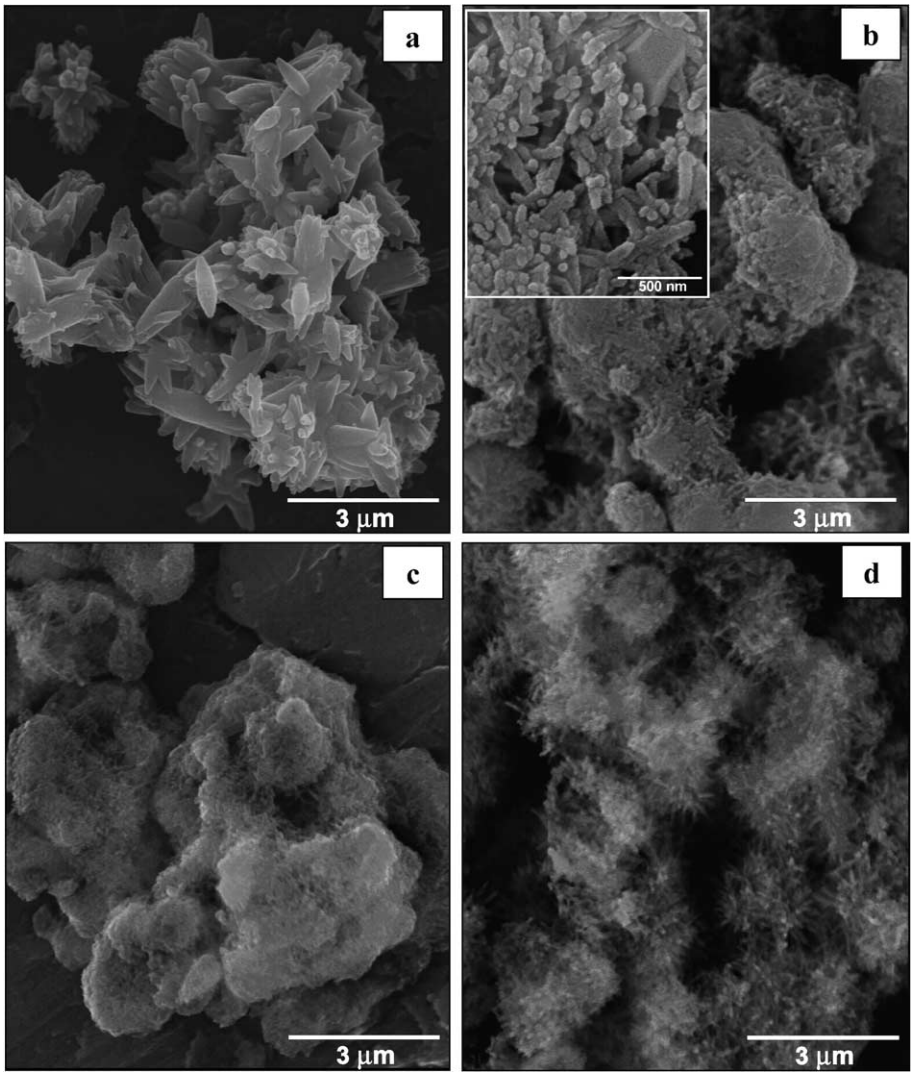

Fig. 2. SEM micrographs of the final calcite particles, obtained at 35 °C, by carbonation of a slaked lime suspension of composition 7.4 wt.% of $Ca(OH)_2$. (a) Blank experiment, (b) 1 wt.% of citric acid, (c) 1 wt.% of sucrose, (d) 1 wt.% of calcium lignosulfonate.

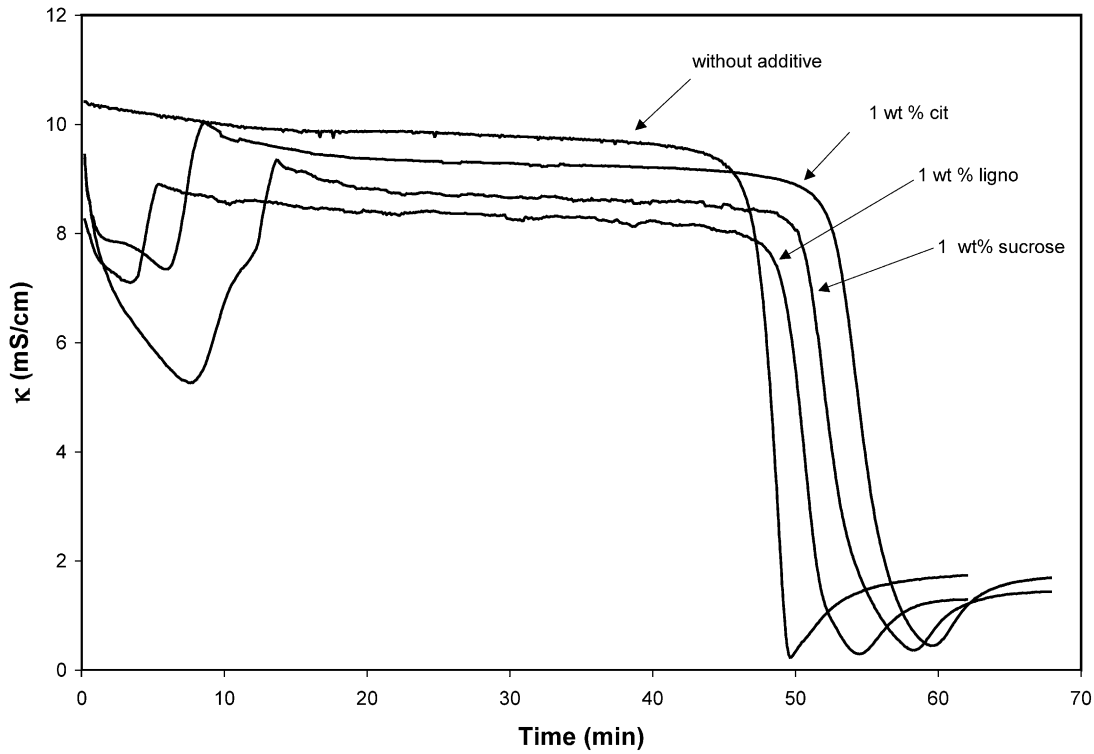

Fig. 3. Evolution of κ during the carbonation of 7.4 wt.% slaked lime at 35 °C, without additives and with additives of group 1 (citric acid, sucrose and calcium lignosulfonate).

3.2. Experiments with additive

Fig. 3 shows the κ-profiles obtained in the carbonation processes in the presence of additives. For a better understanding, only the graphs corresponding to 1 wt.% sucrose, 1 wt.% cit and 1 wt.% ligno, containing a "valley" at the beginning of the carbonation, have been represented. These additives will be denoted as "group 1". The graphs corresponding to the other additives, that is, 0.5 wt.% aerosol OT, 0.5 wt.% sulfate, 1 wt.% sds and 1 wt.% pegl, denoted as "group 2", show an initial plateau similar to that shown in the blank experiment. Only a modification of the duration of the experiments necessary to neutralize the same quantity of slaked lime was produced with respect to the time consumed in the blank experiment.

Table 2 summarizes the relevant operating conditions and the results of these experiments where calcite was the unique precipitated phase. The major differences between them are the obtention of very fine calcite particles with a high specific surface area (SSA) in the range between 26 and 53 m^2/g, in experiments using additives of group 1. These precipitates are difficult to filtrate. SEM observations (Fig. 2b–d) show the presence of chain-like particles, i.e. elongated agglomerates composed by pseudo spherical primary particles within the nanometric size range (see magnified view of Fig. 2b). In experiments using additives of group 2

Table 2
Operative conditions and results of the carbonation experiments of slaked lime

Run	Additive[a]	t^b (min)	SSA (m^2/g)	Modal size D_{50} (μm)	XRD	Morphology[c]
1	–	50	8	8.3	C	scalenohedral
2	1% cit	59	53	5.2	C	elongated agglomerates
3	1% sucrose	58	33	8.0	C	elongated agglomerates
4	1% ligno	54	26	13.0	C	elongated agglomerates
5	1% sds	73	18	8.3	C	scalenohedral
6	5% sulfate	49	13	5.2	C	scalenohedral
7	1% petgl	37	11	6.9	C	scalenohedral
8	0.5% aerosol OT	65	8	6.9	C	scalenohedral
9	1% tie	50	7	6.3	C	scalenohedral

Concentration = 7.4 wt.% Ca $(OH)_2$. Gas flow rate = 7.5 l/min, T = 35 °C.

[a] Concentration based upon the weight of $CaCO_3$ to be produced.

[b] Duration time of the carbonation experiments.

[c] Elongated agglomerates are similar to the chain-like particles in Ref. [5].

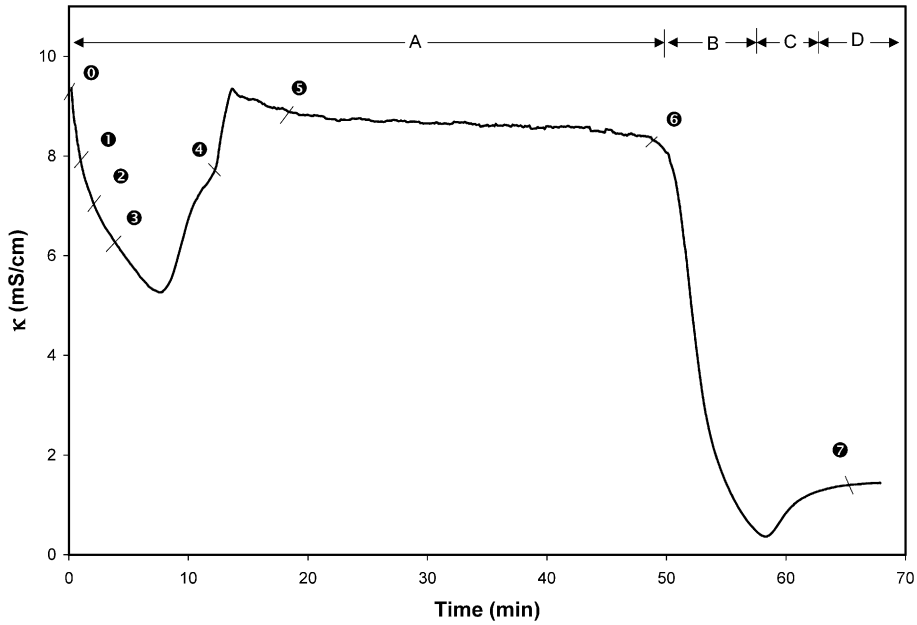

Fig. 4. Evolution of κ during run no. 3, in the presence of 1 wt.% sucrose. Samples 0–7 were taken in the represented points.

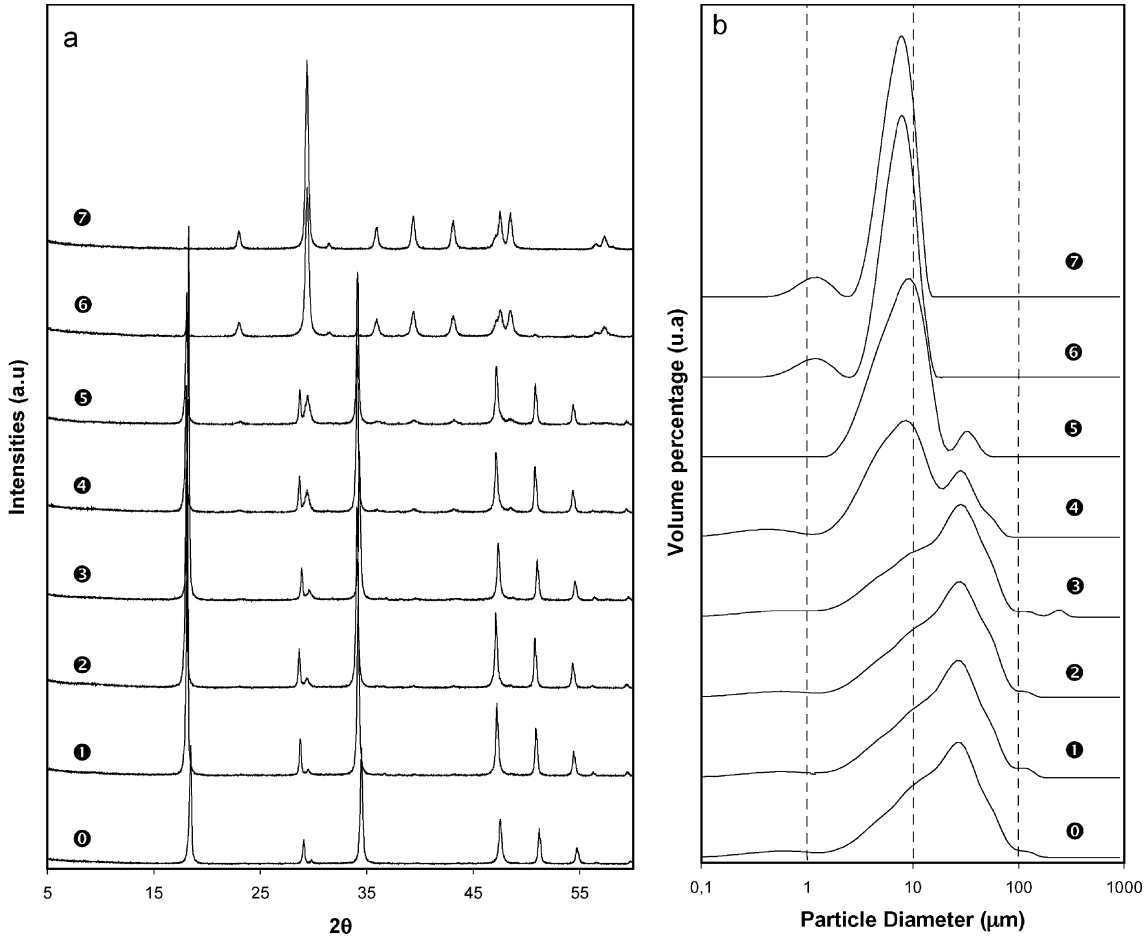

Fig. 5. Evolution of (a) XRD spectra and (b) CSD during run no. 3, carried out in the presence of 1 wt.% sucrose. Samples 0–7 were taken as denoted in Fig. 4.

we obtained calcite particles displaying scalenohedral habit, within the submicrometric/micrometric size range. The SSA of these precipitates, similar to that of particles obtained in the blank experiment (Fig. 2a), ranged between 7 and 18 m^2/g.

During the course of the experiments using additives of group 1, and coinciding with the length of the "valley", it was observed an increase in the viscosity of the suspension produced by the formation of a white gelatinous product. However, at the end of the "valley" the system recovered the appearance of normal suspension. To analyze the evolution of this set of experiments, we selected as model the experiment number three carried out in the presence of 1 wt.% sucrose. In this run some samples were taken at different times (Fig. 4), treated and characterized in a similar way than the final suspension. Fig. 5a shows the evolution of their XRD spectra with time. The diffractogram of the first sample, noted by "0", collected just after the start of the experiment, corresponds to $Ca(OH)_2$. The small reflection peak at $2\theta = 29.46°$ corresponds to an impurity of calcite existing in the initial slaked lime. As shown in this figure, there are no significant changes in the X-ray diffraction diagrams of samples 0 to 3, taken in the descending zone of the κ-valley. After this zone, the calcite content in the suspension increases, whereas the $Ca(OH)_2$ content decreases until zero in sample no. 7 (see the evolution of the representative peak of $Ca(OH)_2$ at $2\theta = 34.06°$). Following this transition by analyzing the CSD (Fig. 5b) we can appreciate that samples 1 to 3 displayed crystal size distributions analogous to that corresponding to the initial $Ca(OH)_2$, with a modal size of 27 μm (sample 0). However, in samples 4 to 7, coinciding with the apparition of the calcite phase, we observe a new and narrower size distribution with a modal size of 8.0 μm.

3.3. Influence of the additive on the CSD

In the present work, it was decided to use the volume-based frequency distribution of the final calcite suspensions, obtained by the Coulter instrument, to analyze the influence of the additives in the aggregation phenomena. Fig. 6 shows the cumulative volume distribution graphs of the different PCCs. It can be observed that the cumulative volume distribution curves corresponding to PCCs obtained using additives of group 2 are quite similar to that of PCC obtained in the blank experiment. These graphs show small shoulders around 1 μm, indicating the bimodal character of the size distribution. However, those graphs corresponding to PCCs obtained using additives of group 1 are different and they do not show any shoulder. To compare among them we have calculated aggregation/dispersion indices defined by Eq. (1) [18]:

$$(D,X)_r = 100[(D,X)_a - (D,X)_b]/(D,X)_b \quad (1)$$

where D is the particle diameter, $X = 10\%$, 50% and 90% is the percentage of cumulative volume undersize distribution (percentage of the population smaller than the size indicated), and subscripts a and b represent the experiments with and without additives, respectively. Thus, $(D,X)_r$ represents the percentage change of the parameter (D,X) produced by the presence of a given additive. A positive value implies aggregation, while a negative one describes the disintegration of aggregates. Thus, $(D,10)_r$ can be interpreted as the volume percentage change associated to fine particles and $(D,90)_r$ as a parameter related with larger sizes. $(D,50)_r$ denotes the relative shift of the size distribution.

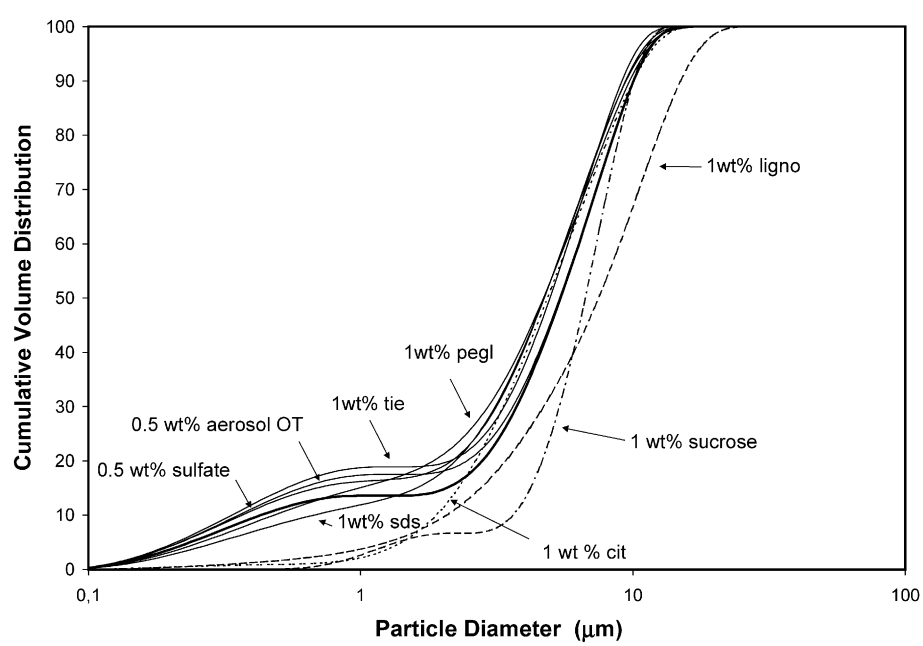

Fig. 6. Cumulative volume distribution graphs of the different PCCs obtained in runs 1–9. Bold line corresponds to run 1 (blank experiment).

Table 3
Aggregation/dispersion indices estimated according to Eq. (1)

Additive	$(D,10)_r$	$(D,50)_r$	$(D,90)_r$
1% cit	341	− 10	0
1% sucrose	741	23	0
1% ligno	381	38	49
1% sds	56	− 13	− 7
0.5% sulfate	− 15	− 13	− 7
1% pegl	11	− 14	− 3
0.5% aerosol OT	− 17	− 1	0
1% tie	− 22	− 8	− 9

Using this criteria we can see in Table 3 that $(D,10)_r$ is a high and positive value when we used additives of group 1 (cit, sucrose or ligno). On the contrary, $(D,10)_r$ is low (positive or negative values) when we used additives of group 2. This finding can be explained by the different individual particle size of the calcite obtained in both cases.

Thus, group 1 additives produce fine chain-like particles (elongated agglomerates of around 150 nm length), which group together to form larger aggregates. In that case $(D,10)_r$ is related with the minimum size of these aggregates. On the contrary, additives of group 2 yield submicrometric/micrometric particles (see the presence of a shoulder around 1 μm in Fig. 6). Here, the index $(D,10)_r$ is mainly related with the individual particle size. In group 1, the analysis of indices $(D,90)_r$ and $(D,50)_r$ revealed that only lignosulfonate displayed a clearly aggregating effect on calcium carbonate in the whole size range. Sucrose and citrate do not affect large-scale aggregation. The additives of group 2, at the used concentrations, weakly promoted the disintegration of aggregates.

4. Discussion

In the present work, two important phenomena, related with the effect of certain commercial additives on the precipitation of $CaCO_3$ at 35 °C, have been observed. Firstly, the additives of group 1 (cit, sucrose and ligno) produce a "valley" at the beginning of the conductivity graphs and yield chain-like particles. Additives of group 2 (sds, pegl, tie, aerosol OT and sulfate) produce conductivity graphs similar to that one produced in the blank experiment, and, like in that case, yield scalenohedral micrometric particles. These findings have not been reported previously for carbonation experiments using additives at temperatures higher than 25 °C. Secondly, the aggregation or dispersion phenomena depend clearly on the type of additives used. Thus, among the additives of group 1 only ligno displayed a clearly aggregating effect in the whole size interval. In this case, $(D,10)_r$, $(D,50)_r$ and $(D,90)_r$ are positive. Sucrose and cit increase aggregation only of the primary particles. On the contrary their $(D,90)_r$ value indicate that they do not affect large scale aggregation. Additives of group 2 showed a small dispersing effect. Only sds and pegl seem to influence aggregation of primary scalenohedral particles.

Previous carbonation experiments made by other authors in absence of additives, at lime concentrations lower than 5 wt.% and temperatures under 30 °C [5,6], showed κ-profiles similar to those obtained in our experiments at 35 °C using additives of group 1. However, these authors reported the formation of colloidal nanometric calcite particles at the end of their experiments. Besides that, during the course of the synthesis they observed the formation of chain-like particles as unstable intermediate products together with unreacted $Ca(OH)_2$ platelets. The chain-like particles transform to the final colloidal nanometric product. In contrast, in our experiments using additives of group 1 we obtained calcite with a chain-like morphology as stable final product. The authors of the cited references suggested that the initial decrease stage of the conductivity (descending region of the valley) is considered to result from the decreasing concentration of dissolved $Ca(OH)_2$ as a consequence of the surface precipitation of tiny particles of amorphous calcium carbonate (ACC), which inhibits the dissolution of the solid lime. In the next period, characterized by the recover of κ, the conversion of ACC to chain-like calcite, an agglomerate in which the primary calcite particles are joined at the crystal faces in a line, probably, by the polarization of particles, takes place. The increase in κ is the result of the removal of the covering material that enables a further dissolution period of $Ca(OH)_2$. In our opinion, the existence of a residual κ value at the end of the descending region of the κ valley, between 5 and 7 mS/cm (see Fig. 3), indicates that the total coverage of the $Ca(OH)_2$ surface by ACC is not complete, and consequently, the inhibition of its dissolution is not completely attained. In addition to this, we think that the formation of a white gelatinous product during this period takes place because the formation of ACC on the lime surface is accompanied by a strong hydration process and by the trapping of OH^- and other components present in the solution, i.e. additives showing a high affinity for the lime surface such as those of group 1. The recovery of κ takes place because the mentioned dissolution period leads to the increase of the concentration of dissolved species such as Ca^{2+}, OH^-, HCO_3^-, CO_3^{2-}, $CaOH^+$, $CaHCO_3^+$, $CaCO_3^0$ and, in our experiments, the anionic form of the additive. The next region is a plateau in the conductivity graph characterized by the presence of chain-like calcite and $Ca(OH)_2$. In this zone chain-like calcite grows at the expenses of dissolved Ca^{2+} and CO_3^{2-} ions. The final drop of κ is produced by the complete consumption of solid $Ca(OH)_2$ particles. Here, chain-like calcite is the only existing solid. Finally, the lowest value of κ marks the end of the carbonation reaction. The authors of Refs. [5] and [6] state that after this point, chain-like calcite separates into individual particles, which grow to a size of about 50 nm.

Comparing our particles with those obtained in Refs. [5] and [6] we observe that our final products are quite similar to their intermediate and unstable chain-like calcite, precursor of the colloidal calcite. However, in our work the chain-like

calcite has been produced at temperatures relatively high, which is very interesting in order to obtain this morphology at the PCC industry. The similarity among the κ graphs reveals that the formation mechanisms are analogous. Thus, group 1 additives or low temperatures ($T \leq 30$ °C) must influence the precipitation of calcite in such a way that the formation mechanism is via chain-like. Our hypothesis is that these agents act in the same way, i.e. decreasing the dissolution rate of calcium hydroxide and subsequently, retaining Ca^{2+} ions near the surface. The presence of dissolved CO_2 leads to a high local supersaturation, which increases the nucleation rate and the number of nuclei. As result, the precipitation of tiny ACC particles, strongly hydrated, takes place over the lime surface. In other words, the presence of these additives increases the stability of ACC and decreases the rate of recrystallization of this amorphous phase.

Füredi-Milhofer et al. [19] found a similar behavior in the formation and transformation of calcium phosphate precipitates obtained by mixing sodium phosphate solutions with calcium chloride solutions in the presence of different additives. These authors confirmed that the use of EDTA and citrate increased the stability of amorphous calcium phosphate (ACP) and decreased its recrystallization rate. In a similar way to the above reported chain-like calcite mechanism, they assume that the calcium phosphate precipitation proceed in at least two steps. First, the formation of relatively stable amorphous colloid dispersions and second the formation of chain-like agglomerates. Following with the analysis of the chain-like calcite formation mechanism, at the beginning of the ACC precipitation the primary particles minimize their surface energy by interacting with the $Ca(OH)_2$ substrate. When the density of these particles on the surface substrate is high enough, the interactions among them become important. In this case, the evolution of the system could be described in a similar way to that proposed by Ocaña et al. [20,21]. Among the different formation mechanisms analyzed by these authors, the process that seems to adjust best in this case is the directional aggregation. Basically, when two tiny particles, in this case of ACC, with characteristic nanometer size, i.e. with an enormous ratio surface/volume, come into contact, a highly relative grain border is created. In the crown formed at the intersection of these two particles, surface diffusion, annealing, and even nucleation is favored. This fact would explain the morphology of the chain-like calcite. The sintering process, and the subsequent reduction of total surface area of the aggregate, can be favored by the desorption of the aggregation-inducting additive, which comes back to the solution and can be used for a new sequence of nucleation–adsorption–aggregation–desorption. Finally, once the slaked lime is consumed, the Ca-additive complexes release Ca ions and then the additive adsorbs onto the chain-like calcite, blocking its transformation to colloidal calcite. This fine calcite exhibits a high tendency toward the formation of aggregates (of modal size around 8 μm) due to their small size and to the aggregating effect of the adsorbed molecules. The aggregation of primary particles most probably takes place by the diminution of electrical surface charge at the end-point of the reaction (see the CSD in Fig. 5b). Therefore, surface charge neutralization is the major factor for the aggregation of this chain-like particles.

Some bibliographic references reinforced our hypothesis about the precipitation mechanism. It was reported that the dissolution rate of calcium hydroxide decreases with the lowering in the temperature [22]. The rate-determining step for calcium hydroxide dissolution is the diffusion of Ca^{2+} and OH^- ions away from the solid–liquid interface, at low stirring speed or the dissolution at the surface at high stirring speed. In the same way, group 1 additives, at the concentration used here, could act, reducing the dissolution rate of $Ca(OH)_2$ by adsorption at the solid-solution interface because of their affinity for surface calcium. For instance, it was reported that adding small quantities of sucrose to the mother liquor in which the slaking of quick lime takes place produce the stabilization of the surface area of $Ca(OH)_2$. This parameter varied when they modified the slaking temperature [23]. At higher sucrose concentrations, the dissolution of $Ca(OH)_2$ can take place by the formation of calcium saccharate [24]. The citrate ions also form strong complexes of Ca-citrate in aqueous solution through their three $-COO^-$ groups. In aqueous suspensions of calcium salts (calcium carbonate, hydroxyapatite) they tend to be adsorbed on the surface calcium employing one or two $-COO^-$ groups [25–27]. Anionic surfactants such as lignosulfonate, a byproduct of the paper industry containing multiple sulfonate and $-CH_2OH$ groups act also as a Ca-complexing agent [23]. Then, it displays certain tendency to be absorbed onto $Ca(OH)_2$ at the solid–solution interface. Finally, the additives containing single sulfonate groups, such us sds, aerosol OT and sulfate or $-OH$ functional groups such us tie or pegl, show a lower tendency to the adsorption on surface Ca^{2+} sites and the changes in the precipitation mechanism are negligible.

At higher temperatures (>30 °C) or using additives of group 2, the dissolution rate of $Ca(OH)_2$ is higher and Ca^{2+} ions tend to be less retained to the surface. Although the formation mechanism of scalenohedral calcite is not yet sufficiently clear, our results are consistent with a nucleation stage and formation of tiny ACC particles produced away from the surface. Transformation of ACC into calcite is very fast and crystal growth of calcite takes place from dissolved CO_2 and Ca^{2+} ions. The dissolution of $Ca(OH)_2$ is progressive and produces a plateau in the whole conductivity graph, until the entire solid $Ca(OH)_2$ consumption.

The study of the influence of these additives in the aggregation of $CaCO_3$ is partial because of the lack of experiments considering the effects of different factors, i.e. concentration, temperature, etc. Therefore, we cannot obtain general conclusions. Nevertheless, under the experimental conditions given in this work, we can distinguish between additives of group 1 (displaying aggregating behavior of primary chain-like particles) and additives of group 2 (displaying a small dispersing behavior of scalenohedral aggre-

gates). In the first case, diminution of electrical surface charge by adsorption of the additives in their anionic forms has been previously argued to be responsible for the primary aggregation. Due to the high specific surface area of these particles, additives are consumed in this part of the process. In the second case, due to the expected lower molecular adsorption, additives do not neutralize surface charge completely. This fact causes the aggregates to weakly disperse by repulsion. The case of lignosulfonate is different because it shows an aggregating influence in the whole size range. Its aggregating effect is explained by the presence of several $-SO^{3-}$ groups per molecule. This polymeric surfactant, derived from the lignin, is used, for instance, as binder to form chemically bonded agglomerates [28].

5. Conclusions

The precipitation of $CaCO_3$ by carbonation of slaked lime at 35 °C is strongly affected by the presence of additives containing carboxylate, multiple sulfonate or $-O^-$ groups such us citrate, lignosulfonate and sucrose. These additives modify the precipitation mechanism in such way that the final individual particles are elongated agglomerates composed by pseudo spherical primary particles within the nanometric size range. These particles are known as 'chain-like'. The use of additives containing single sulfonate groups or $-OH$ groups such us sodium dodecyl sulfate, calcium sulfate hemihydrate, polyethylene glycol 300, sodium dioctyl sulfosuccinate, and triethanolamine do not modify the precipitation mechanism, and yield scalenohedral particles in the submicrometric/micrometric size range. These final particles are similar to those particles obtained in the absence of additives. A possible explanation has been given in terms of the different effects of these additives in the dissolution rate of $Ca(OH)_2$ as well as in terms of their inhibitory role in the chain-like to colloidal calcite transformation.

On the other hand, sucrose, citric acid and calcium lignosulfonate displayed an aggregating behavior of the primary chain-like particles. In addition to this, ligno has been the only additive displaying a clearly aggregating effect in the whole size range. The other additives, at the concentrations used here, showed a small dispersing effect.

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