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Precipitation of super-fine calcium carbonate by controlled double jet method: solid phase characterization and estimation of kinetic parameters

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Super – fine calcium carbonate was prepared by double jet precipitation method. The values of the estimated kinetics parameters show that nucleation is the dominant mechanism in all experimental runs.

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1. Introduction

Calcium carbonate, a wide spread mineral, used in many fields of activity (constructions, paper manufacturing, cosmetics, pharmaceutics) is still very interesting due to the new possibilities raised by the development of nanotechnology. Nano calcium carbonate finds applications in advanced materials like composites and biomaterials.

Calcium carbonate used in industry may be classified according to its particles properties and preparation method into limestone powder, ground calcium carbonate and precipitated calcium carbonate (PCC).

The deposition of solid particles from the liquid phase through a precipitation reaction is a simple and reliable method for obtaining nanostructures with good control of particles' characteristics. Several studies have been published regarding the synthesis of metal oxides, hydrous oxides and hydroxide particles by precipitation from aqueous solutions [1, 2].

The controlled double-jet precipitation method allows the production of colloidal particles with a good control of their monodispersity [3].

Chemical and biological precipitation of calcium carbonate polymorphs have been studied in some details [4]. Recently it was described how different calcium carbonate precipitates were obtained in solutions of calcium salts by catalytic decomposition of urea at 90°C [5].

Enzymes can yield various calcium carbonate polymorphs and influence the development of different habits of calcite [6].

The precipitation of calcium carbonate by liquid-liquid reaction usually provides a mixture of polymorphs since calcium carbonate has at least three stable polymorphs: calcite, aragonite and vaterite. In order to induce the crystallization of aragonite, the high pressure polymorph, the precipitation conditions, such as supersaturation, temperature, pH, feeding order, stirring, additives, must be carefully controlled.

It is known that organic molecules or polymers can influence the crystallization of inorganic salts and may act as crystal growth inhibitors. Crystallization process may be controlled by various additives [7]. It is not yet clear if the additive interacts with dissolved components or with the developing phase.

Ultrasounds may also affect the process. Complex phenomena take place in liquids when an ultrasonic field is applied. It is assumed that diffusion processes are accelerated and particles agglomeration is prevented. Ultrasounds yield cavitation bubbles which accumulate gases and vapors from the liquid phase until they become too large and collapse, producing shock waves. The temperature and pressure inside the cavitation bubbles and in their vicinity are huge and influence all chemical reactions taking place in the liquid phase. It was estimated that the temperature of these hot spots rises as high as 5000°C comparative with the solar temperature and the pressure gets to 1000 atm. Because bubbles dimensions are so small in comparison with the surrounding liquid, heat dissipates quickly enough that macroscale conditions are not disturbed. This combination of high temperatures and pressures and quick cooling determines special conditions for the chemical reactions. The intense forces generated by the collapse of cavitation bubbles can result in significant secondary nucleation. The mechanism by which crystal growth is influenced is less understood but it is probably linked to the effect of acoustic streaming which enhance mass transfer close to the crystal surface. It is assumed that ultrasonic waves can intensify heat

transfer, nucleation rate and growth rate of crystals. They influence particles size distribution and agglomeration process [8]

This paper reports the synthesis of aragonite, the high pressure polymorph of calcium carbonate, in liquid-liquid reaction by the double jet precipitation method. The reaction medium was either bi-distilled water or a solution of bi-distilled water and ethanol. The influence of ultrasonic agitation on the particle size distribution was investigated in comparison with magnetic stirrer.

The final PSD, measured in a mass base system, on a laser beam particle size analyzer (PSA) was used for the kinetic parameter estimation considering that the final shape of the PSD is the result of overlapping primary and secondary crystallization mechanisms such as nucleation, growth and agglomeration. The parameters were estimated by fitting the experimental PSD to the computed values obtained by solving the population balance equation as defined in a large number of publications [9-11].

2. Experimental

Aragonite was synthesized by liquid-liquid reaction using 0.1 M solutions in bi-distilled water of analytical grade, calcium nitrate tetrahydrate (Riedel-de Haen) and potassium carbonate (Sigma-Aldrich). The reagents were introduced into a glass reactor by means of peristaltic pumps at the same flow rate of 10 ml/min. The reaction medium was either 50 cm^3 of bi-distilled water or a mixture of water and ethanol 1:1in volumes. The reaction temperature was kept constant at 50°C by means of a thermostate.

In a first set of experiments a magnetic stirrer performed the agitation into the reaction medium. In a second set of experiments the glass reactor was placed into an ultrasonic bath and agitation was resumed to the influence of ultrasonic field.

The precipitate was aged for 1hour, then filtered and washed several times with bi-distilled water and dried at 100°C.

Table 1 presents the reaction conditions and the main properties of the precipitates.

Table 1. Experimental results.

Sample	Agitation	Reaction medium	FT-IR and XRD	Mean diameter PSA [μm]	XRD Mean diameter [nm]
A 1	magnetic	50 cm^3 bi-distilled water	65.05% aragonite; 2.78% calcite; 32.17% vaterite	15.314	102; 190; 60.7
B 1	magnetic	50 cm^3 ethanol – water 1:1	98.76 % aragonite; 1.24 % calcite;	1.457	25.4 33.3
A 2	**US** 50 kHz;	50 cm^3 bi-distilled water	71.48% aragonite; 20.99% calcite; 7,53% vaterite	13.282	57.5; 570; 47.9
B 2	**US** 50 kHz;	50 cm^3 ethanol – water 1:1	98.18 % aragonite; 1.82 % calcite	1.075	18.2 21.2

Phase composition was established by FT-IR spectroscopy using a Perkin-Elmer spectrophotometer. PCC samples were dispersed in spectral grade KBr and pressed. Using powder X-ray diffraction (diffractometer Bruker D8 Advantage) quantitative phase composition was established and particles mean size was calculated with Debye-Scherrer formula. Particle size distribution was also investigated using a laser beam particle size analyzer (Analysette 22 Micro Tech). TEM was performed using a JEOL 200CX electron microscope. Samples were deposited on carbon coated 3 mm diameter copper electron microscope grids.

3. Mathematical modeling

Based on the population balance equation, a mathematical model was derived and solved to sustain the mechanisms assumed for the particles generation and growth. It is considered that in the present experimental conditions the feed streams are instantaneously mixed due to the reduced reaction volume and efficient agitation means. As in any precipitation process there are four main steps involved: chemical reaction, nucleation, growth and agglomeration, that overlap and define the final PSD. The simultaneous addition of chemical reagents, at equal flow rates and in intense mixing conditions, allows considering a constant supersaturation level all over the reaction time and hence constant nucleation, growth and agglomeration rates during the precipitation. The main parameters defining the rates of these processes were estimated using a nonlinear regression technique to fit the computed PSD with the experimental distribution measured at final reaction time. The goal of mathematical modeling is to confirm the mechanisms involved in particles generation and growth and to provide a tool in predicting the PSD in the precipitation of calcium carbonate polymorphs.

The non-steady state population balance for double jet precipitation, considering a characteristic crystal size *L,*

can be written in terms of population density function *n(L,t)*, as an integro-differential equation:

$$\frac{1}{V(t)}\cdot\frac{\partial(V(t)\cdot n(L,t))}{\partial t}+\frac{\partial(G(L,t)\cdot n(L,t))}{\partial L}=B^0(t)\cdot\delta(L-L^*)+r_A(L,t) \quad (1)$$

where *V(t)* is the suspension volume at moment *t*, *G(L)* is the growth rate, B^0 the nucleation rate and $r_A(L,t)$ is the agglomeration rate defined as:

$$r_A = B(L,t) - D(L,t) \quad (2)$$

where *B(L,t)* is the birth function and *D(L,t)* is the death function calculated by the integrals:

$$B(L,t)=\frac{1}{2}\int_0^L \beta\cdot n(L-y,t)\cdot n(y,t)dy \quad (3)$$

$$D(L,t)=\int_0^\infty \beta\cdot n(L,t)\cdot n(y,t)dy \quad (4)$$

In equation (1) the Dirac symbol defines the nucleation only at nuclei size, L^* (δ=1 if $L=L^*$ and δ=0 if $L\neq L^*$). The agglomeration kernel β stands for the kinetic constant in the agglomeration rate, and is considered to be size independent: we assume small and large particles to have the same chance to efficiently collide and generate agglomerates in a well agitated suspension. The size independent agglomeration kernel was generally proved to be a suitable choice for precipitation processes and especially in the case of sparingly soluble salts (calcite, vaterite, calcium oxalate) [12-15]. The population balance equation was integrated using a discretization method based on the concept of classes as defined by Marchal et al [16]. According to this method the particle size range is divided into *k* classes of amplitude $\Delta L_i = L_i - L_{i-1}$ and characteristic size $\overline{L_i} = (L_i + L_{i-1})/2$ and the PSD equation was transformed into an ordinary differential equation system by defining for each class the number of particles at time *t* per unit volume as:

$$N_i(t)=\int_{L_{i-1}}^{L_i} n(L,t)dL \quad (5)$$

The net particle generation by agglomeration in class "*i*" is calculated by integrating the agglomeration rate over the class size:

$$R_{A,i}(t)=\int_{L_{i-1}}^{L_i} r_{A,i}(t)dL \quad (6)$$

The classes were generated with the ratio $L_i / L_{i-1} = 2^{1/3}$ and, consequently, the contribution to the PSD of the agglomeration caused by the collision of two particles with sizes L_i and L_j, was evaluated by the relation derived by Hounslow et al [17]:

$$R_{A,i}=N_{i-1}\sum_{j=1}^{i-2}2^{j-i+1}\beta\cdot N_j+\frac{1}{2}\beta\cdot N_{i-1}^2-N_i\sum_{j=1}^{i-1}2^{j-i}\beta\cdot N_j-N_i\sum_{j=i}^{\infty}\beta\cdot N_j \quad (7)$$

Considering the approximation consisting in a simple numerical calculation of the population density function: [16]:

$$n(L_i)\approx\frac{\frac{N_{i+1}}{L_{i+1}-L_i}+\frac{N_i}{L_i-L_{i-1}}}{2} \quad (8)$$

the following system of *k* differential equations is generated:

$$\frac{dN_1}{dt}+\frac{1}{V}\frac{dV}{dt}N_1+\frac{G(L_1)}{2(L_2-L_1)}N_2+\frac{G(L_1)}{2(L_1-L_0)}N_1=B^0+R_{A,1} \quad (9)$$

$$\frac{dN_i}{dt}+\frac{1}{V}\frac{dV}{dt}N_i+\frac{G(L_i)}{2(L_{i+1}-L_i)}N_{i+1}+\frac{G(L_i)-G(L_{i-1})}{2(L_i-L_{i-1})}N_i-\frac{G(L_{i-1})}{2(L_{i-1}-L_{i-2})}N_{i-1}=R_{A,i}$$
$$i=2,\ldots k-1 \quad (10)$$

$$\frac{dN_k}{dt}+\frac{1}{V}\frac{dV}{dt}N_k-\frac{G(L_{k-1})}{2(L_N-L_{k-1})}N_k-\frac{G(L_{k-1})}{2(L_{k-1}-L_{k-2})}N_{k-1}=R_{A,k} \quad (11)$$

With the initial conditions:

$$t=0,\quad N_i=0\quad \mathrm{i}=1,\ldots\mathrm{k}$$

These equations were solved using a Runge-Kutta type method considering also the further assumptions and consideration:

- The generation function termed as nucleation represents in this model the particle generation within the first class, defined by the smallest crystal dimension that enters in the field of view of the PSA.
- Size dependent growth rate of power law type, according to the ASL model [18]: $G(L)=G_0\cdot(1+a\cdot L)^b$, where G_0 is the growth rate at zero particle size.
- Reagents are added at flow rates Q_1 and Q_2 meaning that $\frac{dV}{dt}=Q_1+Q_2$
- The suspension volume at time *t* is calculated as: $V(t)=V_0+(Q_1+Q_2)\cdot t$ and V_0 is the initial volume of water or water-ethanol solution in the reaction vessel.
- The suspension is perfectly mixed from the macroscale point of view.

The kinetic parameters B^0, G_0, β and the ASL model constants *a* and *b* have to be adjusted from the correlation

of experimental PSD data obtained at final reaction time. The parameters are estimated by minimizing the objective function:

$$F = \sum_{i=1}^{k} [\ln(N_{i,\exp}) - \ln(N_{i,comp})]^2 \quad (13)$$

The minimization is carried on using a random optimization procedure defined by Luus and Jaakola [19] which is efficient for the minimization of multimodal objective functions, a characteristic feature in kinetic parameter estimation.

The experimental number of particles, $N_{i,\ exp}$ is calculated from the mass base PSD with the relation:

$$N_i = \frac{[M(L_i) - M(L_{i-1})] \cdot m_T}{\overline{L}_i^3 \cdot \rho_s \cdot k_v}, \quad (14)$$

where $M(L)$ represents the experimental cumulative mass distribution, m_T the final suspension density meaning mass of solid phase per unit volume, ρ_s is the solid phase density and k_v the volumetric shape factor. The numerical values considered are ρ_s=2900 kg·m^{-3}, m_T=4 kg·m^{-3}, calculated from overall mass balance considering the reaction complete. The shape factor was estimated by microscopic investigation of particles obtained in each of the four experimental conditions and has values between 0.7 and 0.8.

The integration of equations (9-11) provides the theoretical PSD expressed by computed number of particles in class "i", $N_{i,\ comp}$. The computed PSD must be consistent with the mass balance, and an additional condition was considered by defining the third moment of the PSD at final reaction time that should represent the total mass of solid phase at final reaction time:

$$\mu_3 = \sum_{i=1}^{k} \overline{L}_i^3 \cdot N_i \quad (15)$$

The mass conservation law can be represented, in a simplified manner by the equation:

$$m_T = \rho_s \cdot k_v \cdot \mu_3 \quad (16)$$

The optimization procedure can lead to various sub-optimal solutions due to the interconnection between parameters. The mass balance equation (equation 16) was used for the selection of the best parameter values.

4. Results and discussion

FT-IR spectroscopy is a reliable method of characterization for precipitated $CaCO_3$ phase composition. Each calcium carbonate polymorph presents characteristic infrared vibration bands. For aragonite the specific bands are: 700, 713, 844, 854, 1083 cm^{-1}. The band at 745 cm^{-1} is assigned to vaterite. Calcium carbonate precipitated at 50°C, proved to be mainly aragonite. The other two anhydrous polymorphs (calcite and vaterite) are present in various ratios (Table 1, Figure 1). XRD measurements confirmed the conclusions drawn on the basis of FT-IR spectra.

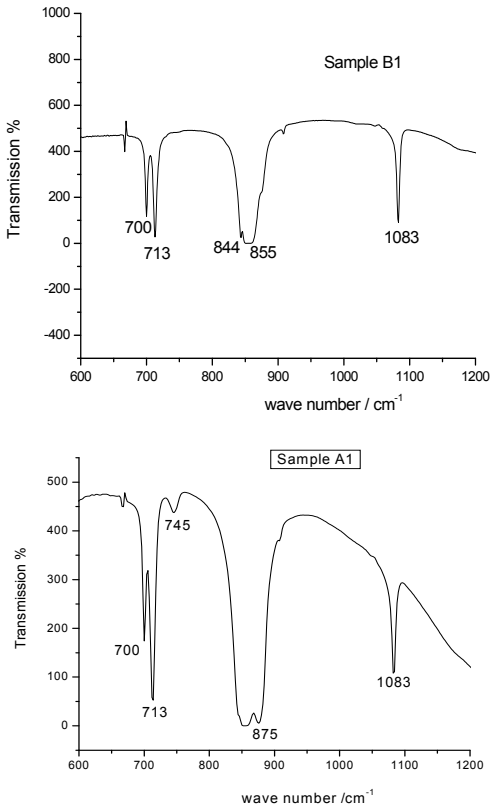


Fig. 1. FT-IR spectra of PCC developed in water (A1) and in a mixture of water-ethanol 1:1in volumes (B1)

The reaction medium proved to have a significant influence on the composition of the precipitate and on the particle size distribution. When the reagents are dropped and react in bi-distilled water, the proportion of the other stable polymorphs of $CaCO_3$ is significant, PCC is a mixture of the three polymorphs, aragonite being still the dominant phase with a percentage of 65-70 %. When the reaction medium is a solution of 1:1 ethanol and bi-distilled water, the phase composition determined both by FT-IR spectrometry and XRD measurements, shows that aragonite is only slightly impurified with calcite (1.24-1.28 %). The temperature of 50 °C is reported to be specific for aragonite development but from our experiments the reaction medium is in fact more important. The presence of short chain alcohols, at 50°C proved to be favorable to aragonite development [20].

The particle size distribution diagram registered by means of a particle size analyzer shows that when the reaction medium was a mixture of ethanol and bi-distilled water 1: 1 in volumes, a diminishing of the particles size by one order of magnitude appears, irrespective of the stirring mode. However, the stirring mode is also important. We noticed that when the reaction took place in ultrasonic field the mean particle size was 15 to 23 % smaller than in the case of magnetic stirring. The PSA (laser beam analyzer) measures in fact not the individual

crystallites size but the size of agglomerates and it registers a mass base distribution, emphasizing the contribution of agglomerates. It is well known that agglomeration of the PCC particles represents a problem. The diminishing of the dimensions when ultrasonic field is used proves that ultrasounds destroy the aggregates in a quite effective manner.

From XRD spectra, using the Debye-Scherrer formula, the crystallites size was estimated using the most intensive maxima for each phase, for the aragonite polymorph, reflexions (111) and (221) and for calcite, reflexion (104) (Fig. 2).

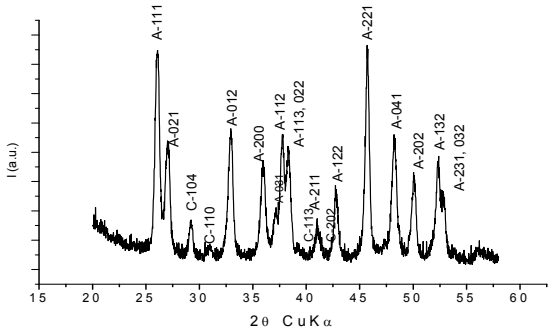
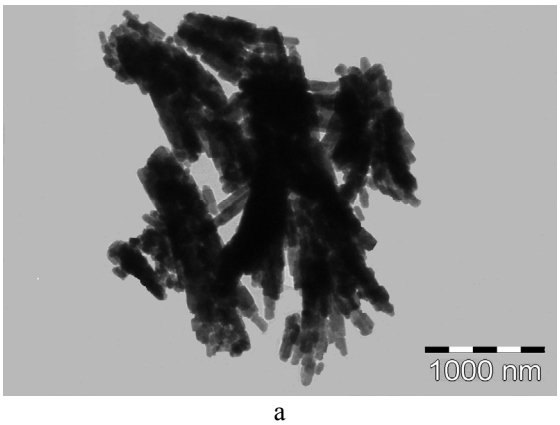
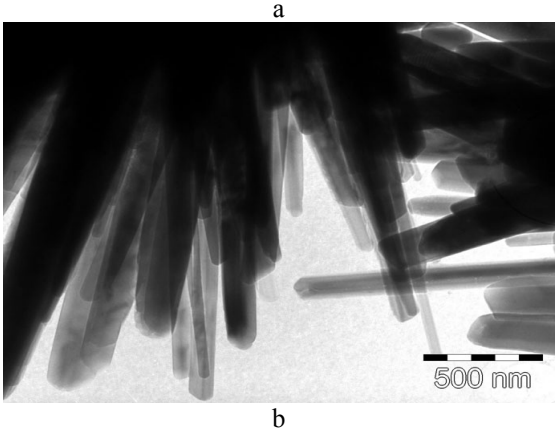


Fig. 2. XRD spectrum of sample B2

These measurements proved that using the double jet precipitation method nanoparticles of PCC develop. In the presence of ethanol and ultrasonic field aragonite dimensions dropped to 18 nm.



a



b

Fig. 3. TEM images of PCC. (a) Sample B2; (b) sample A2.

TEM images reveal the presence of nanometric particles gathered in agglomerates of micrometric dimensions (Figure 3a) in the case when ethanol is present in the reaction medium. When bi-distilled water is used as reactiom medium longer aragonite needels of several microns form and gather in bunches (Figure 3b).

The stirring by means of ultrasounds bath contributes to the development of rod like particles instead of needle like particles developed with magnetic stirrer.

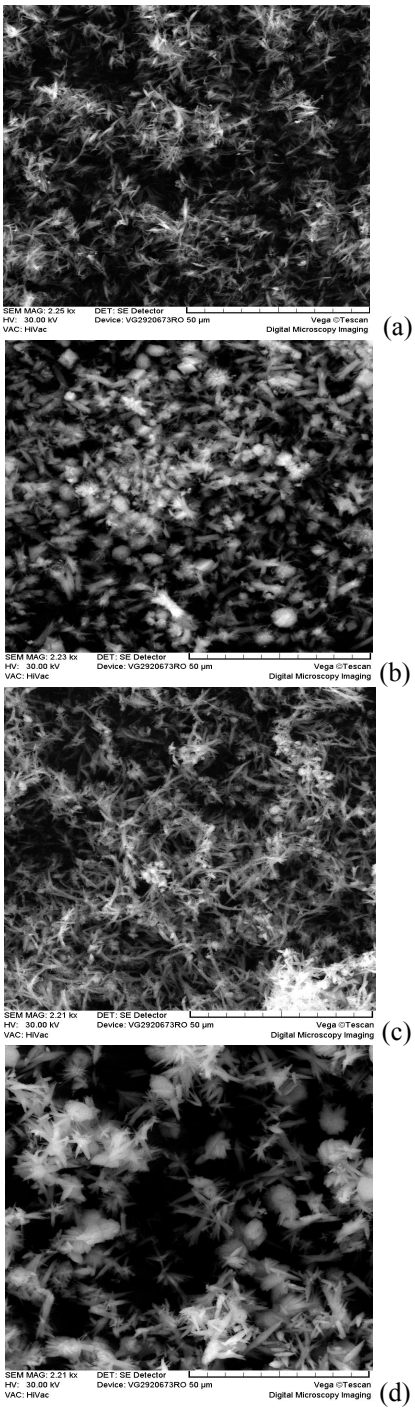


Fig. 4. SEM images for PCC. (a) Run B1, (b) Run A1, (c) Run B2, (d) Run A2

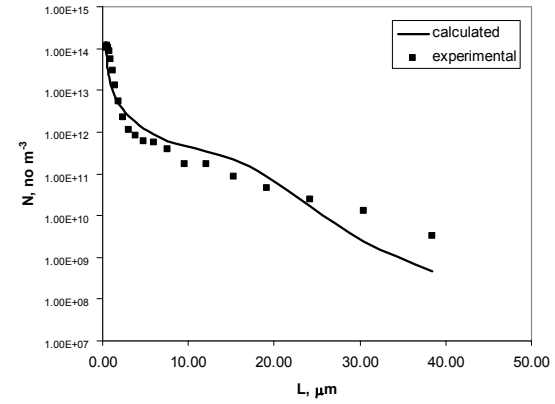
Fig. 4 presents SEM images of the PCC obtained in the four experimental runs. The images show a significant contribution of spherical vaterite and calcite in run A1 (figure 4b) and A2 (figure 4d) while in run B1 (figure 4a) and run B2 (figure 4c) mainly rod and needle like aragonite are present.

The estimated values of kinetic parameters are presented in Table 2.

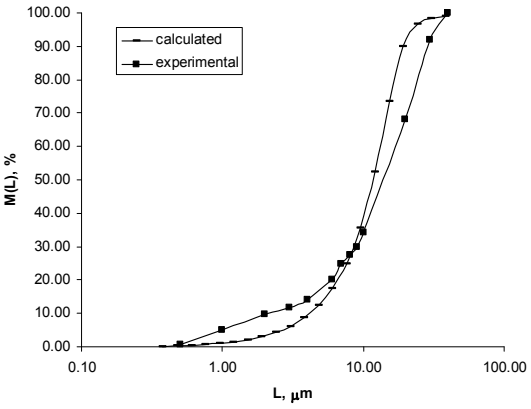
Table 2. Estimated kinetic parameters

Run	B^0, no·m^{-3}s^{-1}	G_0, m·s^{-1}	a, m	b	β, m^3·s^{-1}	F_{min}	Error in mass balance, %
A1	1.8625×10^{14}	1.3297×10^{-11}	3.91×10^{7}	0.278	4.4159×10^{-15}	12.2	23.1
B1	4.0002×10^{14}	1.1597×10^{-10}	2.45×10^{5}	0.098	1.0578×10^{-17}	3.67	2.0
A2	6.2148×10^{14}	2.1678×10^{-10}	2.74×10^{7}	0.47	2.1678×10^{-15}	16.4	27.5
B2	4.0789×10^{14}	2.36×10^{-10}	4.89×10^{7}	0.017	3.27×10^{-18}	2.35	1.2

It may be noticed from the data in Table 2 that the mathematical model gives more reliable results in the case of ethanol-water precipitation medium where few agglomerates are formed. In this case the constant mean shape factor considered from the transformation of mass based PSD into number based distribution introduces lower errors. On the other hand when large agglomerates are formed, the constant kernel agglomeration model might not be enough accurate to capture the complexity of the process. Figs. 5-8 present calculated and experimental PSD data.

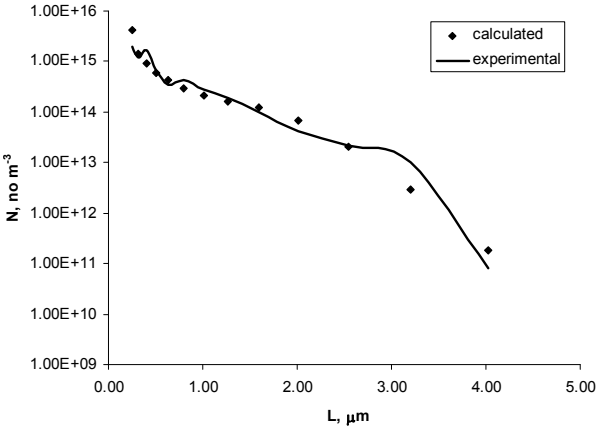


Number of particles per unit volume

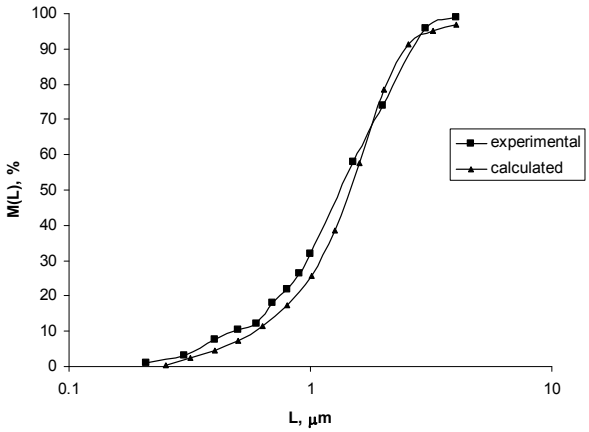


Mass based cumulative PSD

Fig. 5 Experimental and computed PSD for A1.



Number of particles per unit volume

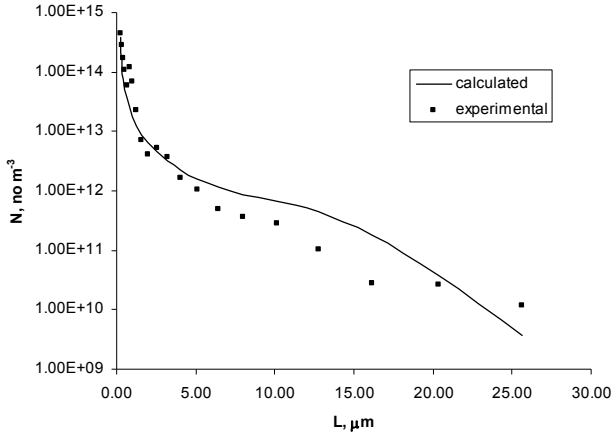


Mass based cumulative PSD

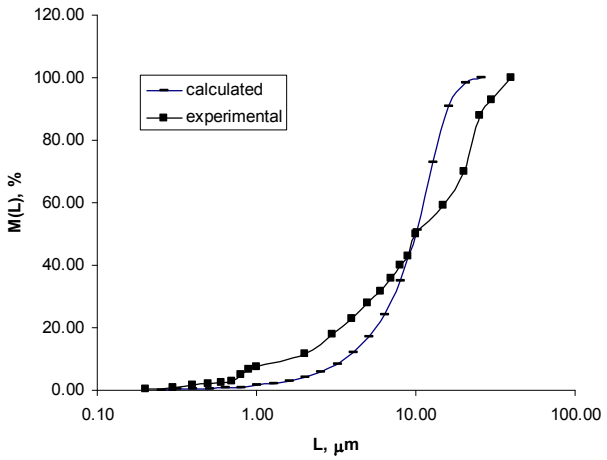
Fig. 6. Experimental and computed PSD for B1.

The data in Table 2 confirm that nucleation is the dominant mechanism in all experimental runs. The ultrasonic filed slightly increases the nucleation rate, more evident for bi-distilled water medium (run A1 versus A2) than for ethanol-water mixture (run B1 versus B2) and decreases the agglomeration. The linear crystal growth rate, G_0 is affected by the US waves as expected, increasing the crystal growth rate probably by an enhanced

mass transfer close to the crystal surface. The linear crystal growth rate has low values and the assumed size dependency is not relevant for precipitation in ethanol-water mixture where the maximum particle size measured by PSA is about 4 μm. In the case of bi-distilled water, where larger agglomerates are formed, a size dependent crystal growth was revealed, as the values of parameters "a" and "b" show (table 2). The effect of the precipitation medium is even more important on the mechanisms involved than the presence of ultrasonic field. The agglomeration rate is drastically reduced in ethanol water mixture. The newborn particles seem to grow mainly by linear growth mechanism while efficient particle collisions leading to agglomerates are very rare

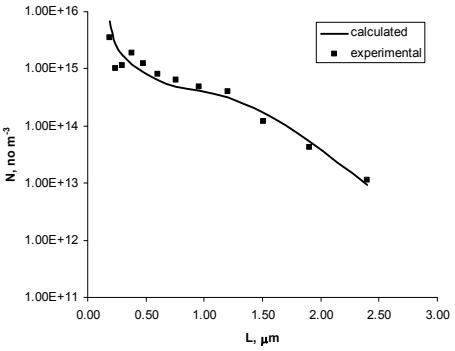


Number of particles per unit volume

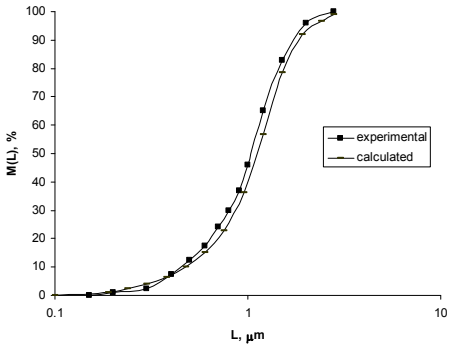


Mass based cumulative PSD

Fig. 7. Experimental and computed PSD for run A2



Number of particles per unit volume



Mass based cumulative PSD

Fig. 8. Experimental and computed PSD for run B2

All experimental runs were carried out at the same reagent concentration and feeding rates. This means that there were no differences concerning the supersaturation level and de-supersaturation rates. This is a possible explanation for the small differences in nucleation rates. Important differences in agglomeration rates are mostly linked to the precipitation medium. This may be explained by the interaction between water and ethanol molecules which can generate associations with properties similar to some organic additives and reduce the possibility of solid particles to efficiently collide. The presence of several polymorphs (runs A1 and A2) may also increase the agglomeration rate by creating a larger free surface of the solid phase capable to attach other solid particles. The polymorphic transformation that probably occurred when the precipitation took place in bi-distilled water may also be responsible for the shape of PSD and a reason for a poorer data fitting with the model based on nucleation, growth and agglomeration.

5. Conclusions

PCC was synthesized by the double jet precipitation method using two mixing systems, either ultrasonic waves or magnetic mixer, in a reaction medium of bi-distilled water or ethanol-water solution.

The presence of ethanol in the reaction medium had an important influence on the final solid phase properties both from morphological point of view and particle size distribution.

The mathematical model derived and the values of estimated kinetic parameters confirm that nucleation is the dominant mechanism in all experimental runs. The agglomeration process is significantly decreased when precipitation takes place in ethanol-water medium.

The double-jet calcium carbonate precipitation in ethanol-water mixtures may be a challenging solution to obtain pure polymorphic phase and submicron size particles.

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