PARTICLE SIZE DISTRIBUTION ANALYSIS FOR CALCIUM CARBONATE PRECIPITATION

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INTRODUCTION

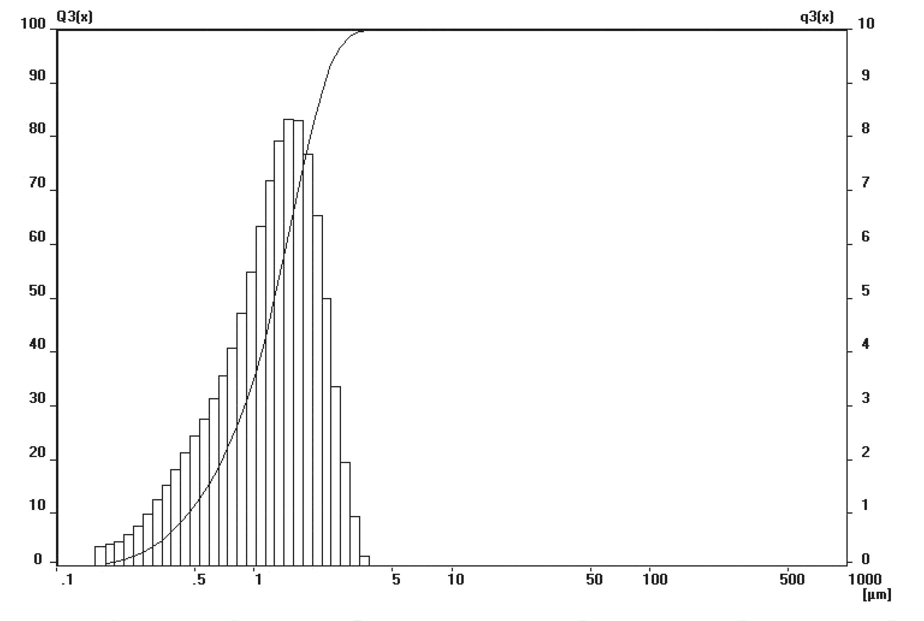
➢The solid phase purity and particle size distribution (PSD) of $CaCO_3$ precipitated by the chemical reaction between two soluble salts and in a gas-liquid system by bubbling CO_2 into a calcium hydroxide were studied experimentally. The main goal was to obtain a pure solid phase with narrow PSD and small mean particle size.

➢The population balance technique, considering homogenous nucleation, size dependent growth and agglomeration was used to model the precipitation process and estimate the parameters that describe the crystallization kinetics.

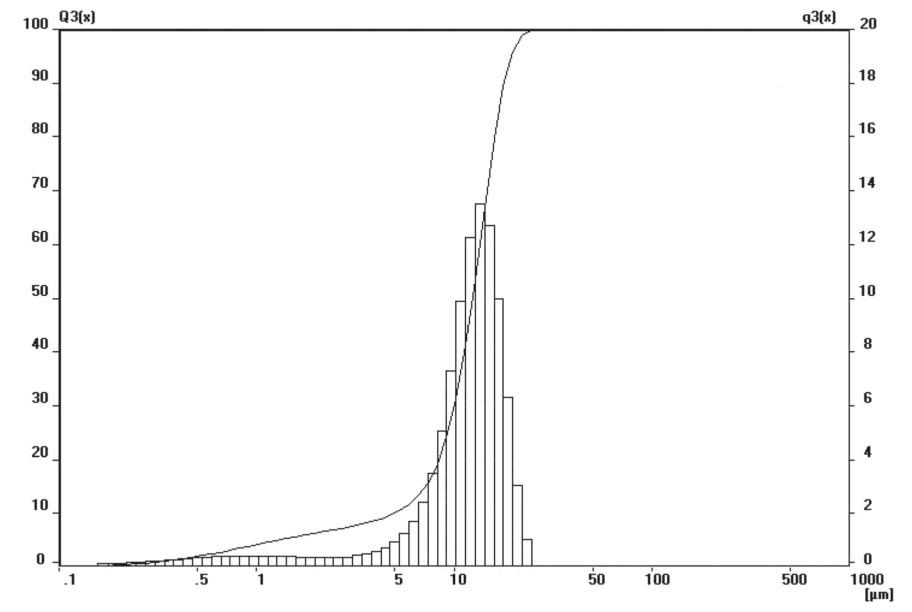
EXPERIMENTAL

Working conditions and experimental results for $CaCO_3$ precipitation

Run	Reaction medium	Reagents concentration	Polymorphs	Mean diameter [μm]
1	bi-distilled water, KCO_3 and $Ca(NO_3)_2$ added in double jet system	0.1 M	Aragonite, vaterite, calcite	15.31
2	ethanol – water ratio 1:1, KCO_3 and $Ca(NO_3)_2$ added in double jet system	0.1 M	Almost pure aragonite	1.46
3	ethanol – water ratio 1:1, KCO_3 and $Ca(NO_3)_2$ added in double jet system	1 M	Almost pure aragonite	6.98
4	bi-distilled water +Tween 20, KCO_3 and $Ca(NO_3)_2$ added in double jet	1 M	Aragonite and vaterite	11.91
5	$Ca(OH)_2$ and CO_2, continuous crystallizer, mean residence time 11 min	2 g/L CaO Pure CO_2	Calcite	7.85
6	$Ca(OH)_2$ and CO_2, continuous crystallizer, mean residence time 22 min	2 g/L CaO Pure CO_2	Calcite	13.8



PSD for ethanol-water mixture (Run 2)



PSD for water+Tween 20 (Run 4)

MATHEMATICAL MODELLING

Population balance equation
$$\frac{1}{V(t)}\cdot\frac{\partial\left[V(t)\cdot n(L,t)\right]}{\partial t}+\frac{\partial\left[G(L,t)\cdot n(L,t)\right]}{\partial L}=B^0(t)\cdot\delta(L-L^*)+r_A(L,t)$$

Growth rate model
$$G(L)=G_0(1+a\cdot L)^b$$

The population balance equation was solved using the method of classes where the PSD is expressed in terms of number of particle in class "*i*", N_i..

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

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

$$\frac{d\,N_i}{dt}+\frac{1}{V}\frac{dV}{dt}N_i+\frac{G(L_i)}{2\cdot(L_{i+1}-L_i)}N_{i+1}+\frac{G(L_i)-G(L_{i-1})}{2\cdot(L_i-L_{i-1})}N_i-\frac{G(L_{i-1})}{2\cdot(L_{i-1}-L_{i-2})}N_{i-1}=R_{A,i}\qquad j=2,\dots m-1$$

$$\frac{d\,N_m}{dt}+\frac{1}{V}\frac{dV}{dt}N_m-\frac{G(L_{m-1})}{2\cdot(L_m-L_{m-1})}N_m-\frac{G(L_{m-1})}{2\cdot(L_{m-1}-L_{m-2})}N_{m-1}=R_{A,m}$$

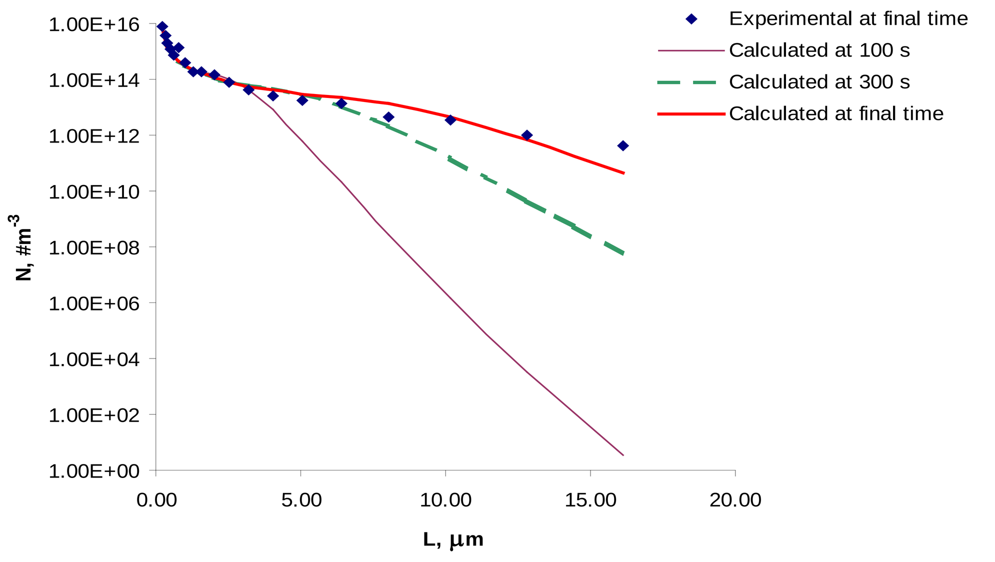
$$R_{A,i}=N_{i-1}\sum_{j=1}^{i-2}2^{j-i+1}\beta\cdot N_j+\frac{1}{2}\beta\cdot N_{i-1}^2-N_i\sum_{j=1}^{i-1}2^{j-i}\beta\cdot N_j-N_i\sum_{j=i}^{\infty}\beta\cdot N_j$$

Objective function for kinetic parameters estimation:

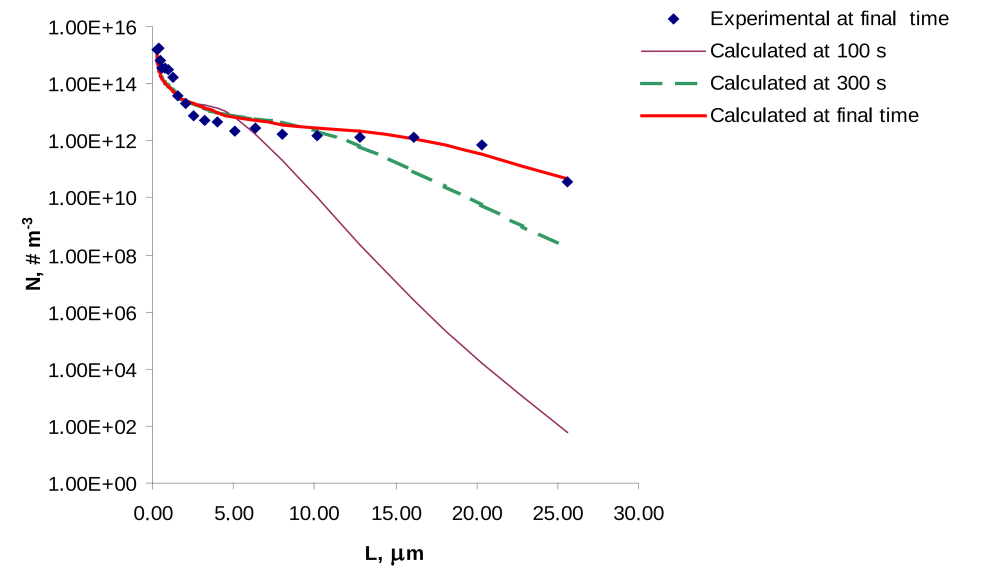
$$F=\sum_{i=1}^{m}\left[\ln(N_{i,\exp})-\ln(N_{i,comp})\right]^2$$

Kinetic parameters

Run	B^0, $\#\cdot m^{-3}s^{-1}$	G_0, $m\cdot s^{-1}$	a, m^{-1}	b -	β, $m^3\cdot s^{-1}$
1	$1.86\cdot10^{14}$	$1.33\cdot10^{-11}$	$3.91\cdot10^{7}$	0.28	$4.42\cdot10^{-15}$
2	$4.00\cdot10^{14}$	$1.16\cdot10^{-10}$	$2.45\cdot10^{5}$	0.10	$1.06\cdot10^{-17}$
3	$5.46\cdot10^{15}$	$1.51\cdot10^{-11}$	$5.60\cdot10^{6}$	0.21	$6.14\cdot10^{-17}$
4	$1.31\cdot10^{15}$	$6.25\cdot10^{-10}$	$6.66\cdot10^{7}$	0.24	$5.32\cdot10^{-16}$



(a)



(b)

Experimental and calculated distributions for 1M reagents concentration in double jet precipitation system:

(a) water-ethanol (Run 3), (b) water +Tween 20 (Run 4).

CONCLUSIONS

➢The operating conditions, such as reagent concentration and additives have significant influence on the final particle size distribution and polymorphic composition.

➢The mathematical model derived proved to correctly represent the mechanisms involved in $CaCO_3$ precipitation.

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