

Model For the Calcite Precipitation with reactants $NaHCO_3 + CaCl_2$

- REWRITE FOR VOLUME BASED!



Conditions:

- Fed-batch operation: continuous additions of $CaCl_2$
- No recycle effects are considered (negligible residency time in the measurement loop)
- The initial carbone is all from $NaHCO_3$ in solution (no equilibrium with CO_2 for now - required to be fixed)

TODO:

- Equilibrium of $NaHCO_3$ and air to adjust initial C concentration;
- Check if use the PSD as size based or mass/volume based (what are the implications for growth and aggregation?)

Mathematical Model

CHECK: use PSD in volume or absolute values ? This will change the PSD by an additional term and the solute consumption due to crystallization.

Population Balance

$$\frac{\partial n(l, t)}{\partial t} + \frac{\partial [G_l(t)n(l, t)]}{\partial l} = \dot{n}_{add}(l, t) + B_0 \delta(l - l_{min}) + R_{l,agg}$$

Or, using the particle volume based distribution:

$$\frac{\partial n(v, t)}{\partial t} + \frac{\partial [G(t)n(v, t)]}{\partial v} = \dot{n}_{add}(v, t) + B_0 \delta(v - v_{min}) + R_{agg}$$

Applying the MSM without particle addition:

$$\frac{dN_0(t)}{dt} = B_0 + R_{agg,0}$$

$$\frac{dN_i(t)}{dt} = R_{agg,i}$$

$$\frac{dx_i}{dt} = G(x_i)$$

$$R_{agg} = \sum_{\substack{i \geq j \geq k \\ j, k \\ x_{i-1}(t) \leq \nu(t) \leq x_{i+1}(t)}} \left(1 - \frac{1}{2}\delta_{j,k}\right) \eta q_{j,k} N_j(t) N_k(t) - N_i(t) \sum_{k=1}^M q_{i,k} N_k(t)$$

$$\eta = \begin{cases} \frac{x_{i+1}(t) - \nu}{x_{i+1}(t) - x_i(t)}, & x_i(t) \leq \nu \leq x_{i+1}(t) \\ \frac{x_{i-1}(t) - \nu}{x_{i-1}(t) - x_i(t)}, & x_{i-1}(t) \leq \nu \leq x_i(t) \end{cases}$$

$$\nu(t) = x_j(t) + x_k(t)$$

Mass Balances for Total species in Liquid Phase

$$\frac{dm_{Ca}}{dt} = Q_{in} C_{Ca,in} + \xi_{Ca} \frac{dm_{c,tot}}{dt}$$

$$\frac{dm_C}{dt} = \xi_C \frac{dm_{c,tot}}{dt}$$

$$\frac{dm_{Na^+}}{dt} = 0$$

$$\frac{dm_{Cl^-}}{dt} = Q_{in} C_{Cl^-,in}$$

$$\frac{dV(t)}{dt} = Q_{in}$$

The rate of consumption of solute to the solid phase for size based is:

$$r_{p,l} = - \left(3 \rho_c k_v \int G l^2 n(l,t) dl \right)$$

However, since it is being working with volume (independent coordinate) based PSD:

$$m_{c,tot} = \rho_c k_v v_{c,t}$$

$$v_{c,t} = \int_0^\infty n(v,t) v dv$$

$$m_{c,tot} = \rho_c k_v \int_0^\infty n(v,t) v dv$$

The derivative is thus:

$$\frac{dm_{c,tot}}{dt} = \rho_c k_v \frac{d}{dt} \left[\int_0^\infty n(v,t) v dv \right]$$

$$\frac{dm_{c,tot}}{dt} = \rho_c k_v \int_0^\infty n(v,t) G(v) dv$$

If PSD is volumetric:

$$m_{c,tot} = \rho_c k_v v_{c,t} V(t)$$

$$\frac{m_{c,tot}}{V(t)} = \rho_c k_v v_{c,t}$$

$$\frac{d \left[\frac{m_{c,tot}}{V(t)} \right]}{dt} = r_p = \rho_c k_v \int_0^\infty n(v,t) G(v) dv$$

The fractions of species are:

$$\xi_{Ca} = \frac{M_{Ca}}{M_{CaCO_3}}$$

$$\xi_C = \frac{M_C}{M_{CaCO_3}}$$

The concentration [g/mL] for species *Ca* and *Cl* in the feed stream are:

$$C_{Ca,in} = \frac{M_{Ca}}{M_{CaCl_2}} C_{CaCl_2,in}$$

$$C_{Cl,in} = 2 \frac{M_{Cl}}{M_{CaCl_2}} C_{CaCl_2,in}$$

Additionally, even though not required to close the ODE system, the added quantity of $CaCl$ can be tracked by:

$$\frac{dm_{CaCl}}{dt} = Q_{in} C_{CaCl, in}$$

Supersaturation Equation

$$S = \frac{\gamma_{Ca^{2+}} x_{Ca^{2+}} + \gamma_{CO^{2-}} x_{CO^{2-}}}{K_{sp}}$$

Equilibrium constant

Equilibrium constant from Torraca thesis for Calcite:

$$K_{sp} = -171.906 - 0.0779T + 2839.319/T + 71.595 \log_{10} T$$

However, they will be obtained from Elvis module (REQUIRES UPDATE):

`calciumcarbonate_supersaturation_module.py`

The equilibrium module from Elvis used molar concentration in $[g/L]$ (CHECK), thus the following auxiliary equations are requires:

Auxiliaries equations

$$m_{slv} = \rho_{mix} V(t)$$

$$\rho_{mix} \approx \rho_w$$

$$c_j = \frac{m_j}{m_{slv}(t)}$$

$$c_{Ca} = \frac{m_{Ca}}{M_{Ca} V_L}$$

$$c_C = \frac{m_C}{M_C V_L}$$

$$c_{Na} = \frac{m_{Na}}{M_{Na} V_L}$$

$$c_{Cl} = \frac{m_{Cl}}{M_{Cl} V_L}$$

Precipitation Kinetics

Growth

Potential References:

- A two-fluid model for calcium carbonate precipitation in highly supersaturated solutions (USED)

$$G(t) = k_g(S - 1)^g$$

From Reis et al. (2018): $g = 2$ and k_g is:

$$\log k_g = -0.275 + 0.228 \left[\frac{I^{1/2}}{1 + I^{1/2}} - 0.3I \right]$$

where I is the ionic strength (mol/L) and $k_g [=] nm/s$.

Verdoes, Kashchiev, and Rosmalen (1992) provides the growth kinetics in a similar form, but with $g = 1.8$ and $k_g = 2.4e - 12m/s$

Nucleation

The conventional equation for nucleation in the form:

$$B_0(t) = k_b(S - 1)^b \mu_3(t)$$

Or, from Reis et al. (2018):

$$B_0(t) = A \exp \left[-\frac{\beta \sigma^3 \nu^2}{2.30 k_b^3 T^3 (\log S)^2} \right]$$

where $\beta = 16.75$ for spherically symmetric particles, $\sigma = 0.068N/m$; $\nu = 6.132 \cdot 10^{-29}$. An approximation for A is given:

$$A = \frac{D}{\epsilon^5 S^{5/3}}$$

$$D = 8.67 \cdot 10^{-10} m^2/s \text{ and } \epsilon = 7.62 \cdot 10^{-10}$$

However, the profile for nucleation using Reis et al. (2018) is not reasonable for the working range of Supersaturation. It is reported a supersaturation of $S = 3235.94$, but the equation for supersaturation is not provided.

Another reference for nucleation of $CaCO_3$ is Verdoes, Kashchiev, and Rosmalen (1992), with the following equation:

$$B_0 = K_s S \exp \left(-\frac{E_b}{\ln^2 S} \right)$$

where $K_s = 1.4e181/m^3/s$ and $E_b = 12.8$

Aggregation

$$q(x_i, x_j) = TODO$$

Conductance

The electrical conductance was estimated from Appelo modified Nernst-Einstein equation (see: <http://www.aqion.de/site/77#Nernst-Einstein>):

$$EC = \sum_i \Lambda_{m,i}^0 (\gamma_i)^\alpha c_i$$

$$\alpha = \begin{cases} 0.6 / |z_i|^{0.5} = const & \text{if } I \leq 0.36 |z_i| \\ \sqrt{I} / |z_i| & \text{otherwise} \end{cases}$$

The values for Λ_0 for each ion is listed in XXX.

Initial Conditions:

PSD:

No Seed at initial time: $N_i = 0$

$$0 \leq x_i \leq 10\mu m$$

Components Concentration and Masses

$$V(0) = 600cm^3$$

$$C_{NaHCO_3}(0) = 1.2275 \cdot 10^{-3}g/cm^3$$

$$m_{Ca^{2+}}(0) = 0$$

$$m_C(0) = \frac{M_C}{M_{NaHCO_3}} C_{NaHCO_3}(0) V(0)$$

$$m_{Na}(0) = \frac{M_{Na}}{M_{NaHCO_3}} C_{NaHCO_3}(0) V(0)$$

$$m_{Cl}(0) = 0$$

Parameters

Operational Conditions

Parameter	Value	Unit
$C_{NaHCO_3}(0)$	$1.2275 \cdot 10^{-3}$	g/cm^3
$C_{CaCl_2, in}$	$0.7275 \cdot 10^{-3}$	g/cm^3
$V(0)^*$	600	cm^3
T	25	$^{\circ}C$
RPM	350	rpm
Q_{in}	1.75	cm^3/min
t_f	56	min

*: confirm initial volume

Physico-chemical parameters

Parameter	Value	Unit
M_C	12.0707	g/mol
M_{Na}	22.99	g/mol
M_{NaHCO_3}	84.007	g/mol
M_{CaCl_2}	110.98	g/mol
M_{Ca}	40.078	g/mol
M_{Cl}	35.453	g/mol
ρ_w	1	g/cm^3

Kinetic parameters

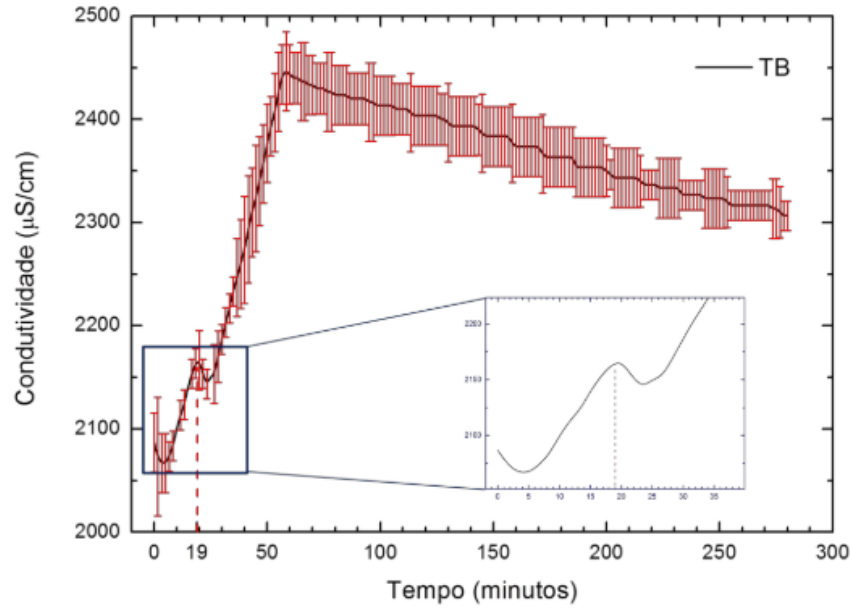
to do

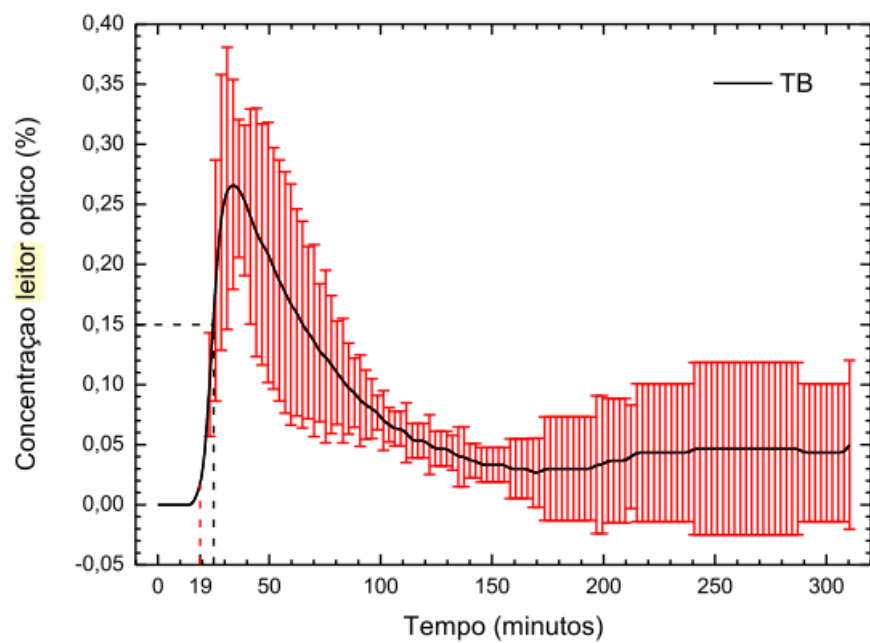
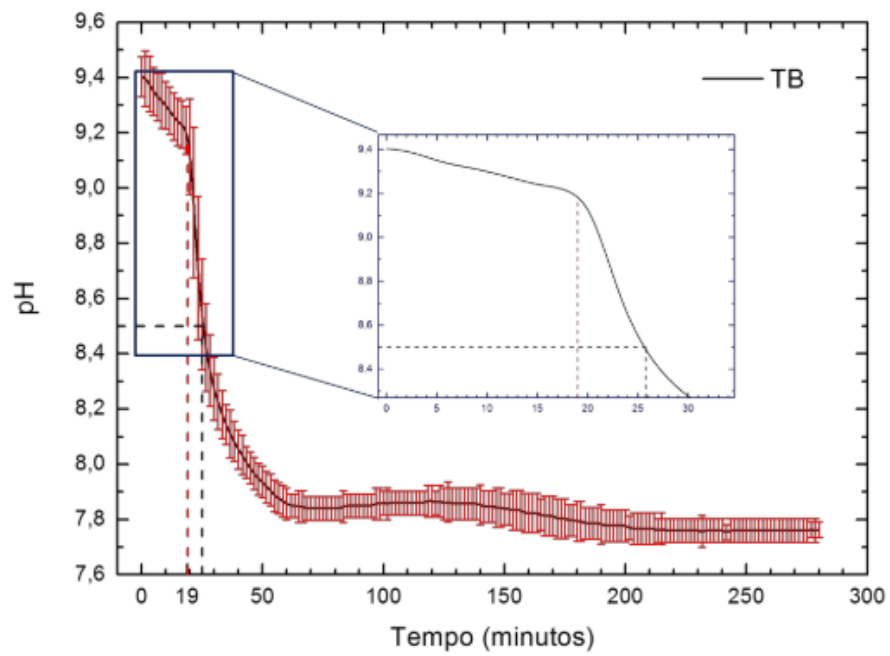
Conductance Parameters

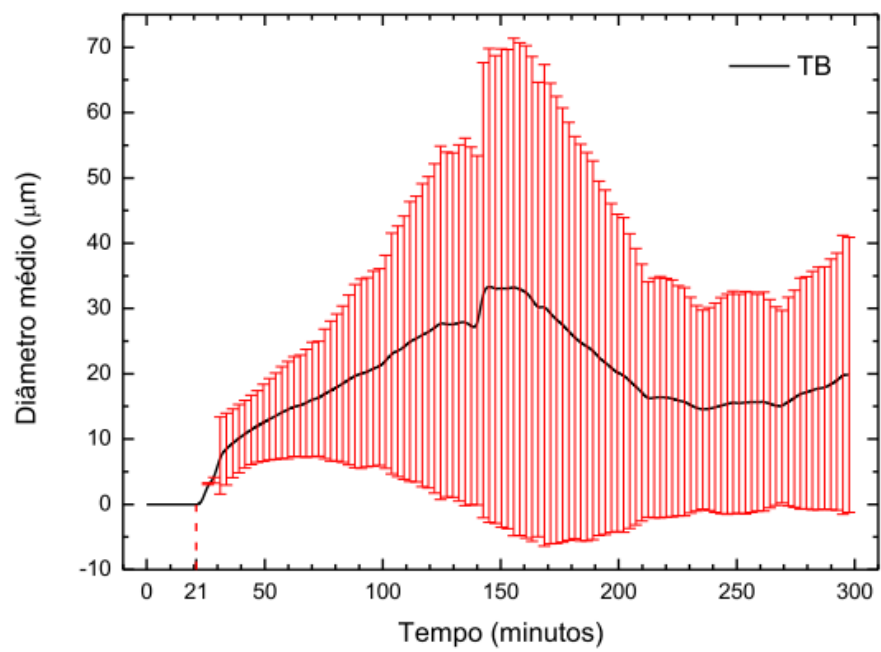
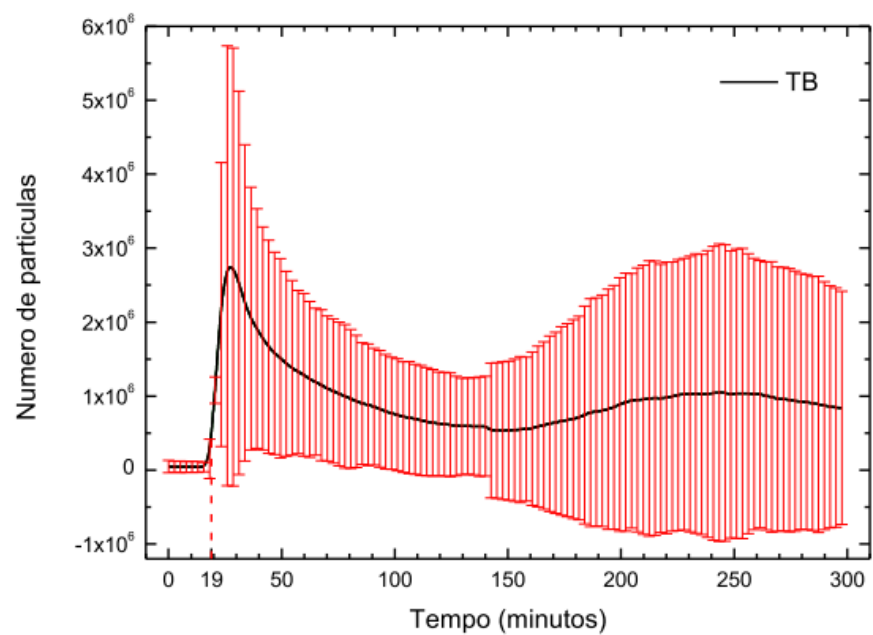
Substance	abs(z)	Di 1e-9 [m ² /s]	$\Lambda_{m,i}^0$ [S cm ² mol ⁻¹]
Na+	1	1.330	50.0
H+	1	9.310	349.6
Ca++	2	0.793	119.1
Cl-	1	2.030	76.2
HCO3-	1	1.180	44.3
NaCO3-	1	0.585	22.0
OH-	1	5.270	197.9
CO3-	2	0.955	143.5
CaOH+	1		
CaHCO3+	1	0.506	19.0

Experimentos - Torraca, 2018

Teste Branco (sem campo magnético)







References

Reis, MC, MFB Sousa, F Alobaid, CA Bertran, and Y Wang. 2018. “A Two-Fluid Model for Calcium Carbonate Precipitation in Highly Supersaturated Solutions.” *Advanced Powder Technology* 29 (7): 1571–81.

Verdoes, D, D. Kashchiev, and G. M. van Rosmalen. 1992. “Determination of nucleation and growth rates from induction times in seeded and unseeded precipitation of calcium carbonate.” *Journal of Crystal Growth* 118 (3-4): 401–13. [https://doi.org/10.1016/0022-0248\(92\)90089-2](https://doi.org/10.1016/0022-0248(92)90089-2).