A model of calcium carbonate scaling on turbulent pipe flows

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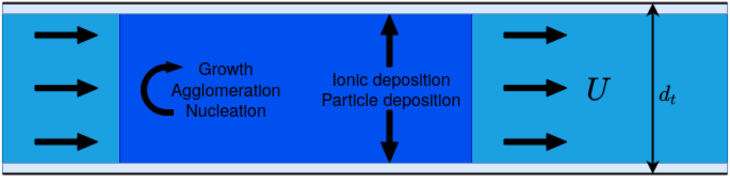


Figura: Schematic diagram of balance model.

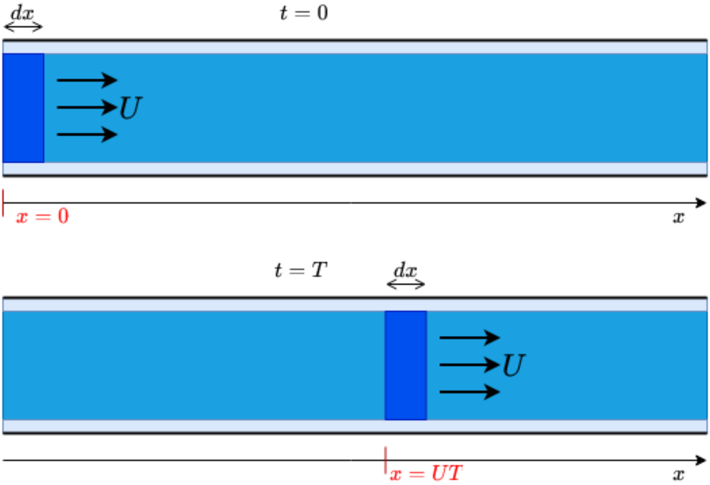


Figura: "Ignoring"the length dimension in our model.

$$\frac{\partial}{\partial t} f(v,t) = \frac{1}{2}\int_0^v B(w, v-w) f(v-w,t) f(w,t) dw - f(v,t)\int_0^\infty B(v,w) f(w,t) dw - \frac{\partial G(v, c_{\mathrm{Ca}}) f(v,t)}{\partial v} - \frac{4}{d_t} L(v) f(v,t) + H(c_{\mathrm{Ca}})\delta(v - \alpha(c_{\mathrm{Ca}})), \quad (1)$$

and (calcium) concentration balance equation

$$\frac{\partial c_{\mathrm{Ca}}(t)}{\partial t} = -\frac{1}{\Gamma}\rho\int_0^\infty G(v, c_{\mathrm{Ca}}) f(v,t) dv - \frac{1}{\Gamma}\rho\alpha(c_{\mathrm{Ca}}) H(c_{\mathrm{Ca}}) - \frac{4}{d_t} J_{\mathrm{CaCO_3}}(c_{\mathrm{Ca}}). \quad (2)$$

The mass deposition rate is then a function of $f(v,t)$ and c_{Ca}

$$\frac{\partial m_x(t)}{\partial t} = \pi d_t \rho \int_0^\infty v L(v) f(v,t) dv + \pi d_t \Gamma J_{\mathrm{CaCO_3}}(c_{\mathrm{Ca}}), \quad (3)$$

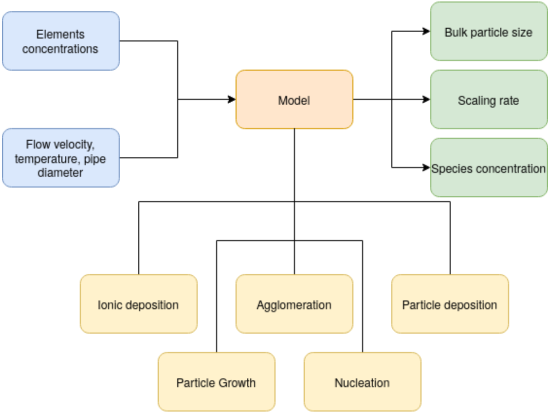


Figura: Schematics of physico-chemical phenomena included in the model

What is *not included*: Scale removal.

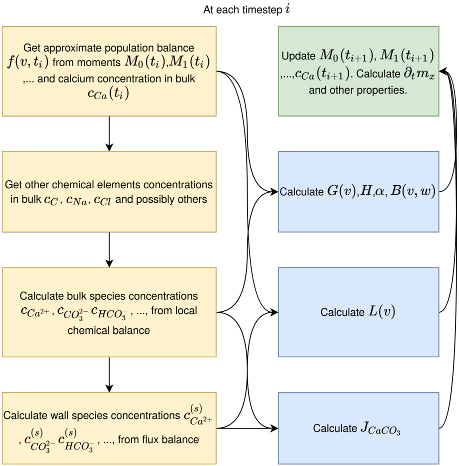


Figura: Schematic diagram of the steps involved at each time step calculation of the ODE.

$$
\begin{aligned}
&Ca^{2+} + {CO_3}^{2-} \leftrightarrow CaCO_3\,(aq)\\
&Ca^{2+} + {HCO_3}^{-} \leftrightarrow {CaHCO_3}^{+}\\
&Ca^{2+} + H_2O \leftrightarrow CaOH^{+} + H^{+}\\
&{HCO_3}^{-} + CO_2 \leftrightarrow H_2O + H^{+}\\
&{CO_3}^{2-} + H^{+} \leftrightarrow {HCO_3}^{-}\\
&H^{+} + OH^{-} \leftrightarrow H_2O.
\end{aligned} \tag{4}
$$

Other reactions appears when considering more elements.

$$
K = \frac{(\gamma_{A_1} c_{A_1})^{a_1} \dots (\gamma_{A_m} c_{A_m})^{a_m}}{(\gamma_{B_1} c_{B_1})^{b_1} \dots (\gamma_{B_n} c_{B_n})^{b_1}}, \tag{5}
$$

Models for activity coefficients γ: Extended Debye-Huckel, Pitzer.
Closing equations: for bulk, electroneutrality and mass balance.

At equilibrium:

$$K_{sp} = \gamma_{\mathrm{Ca}^{2+}} c_{\mathrm{Ca}^{2+}} \gamma_{\mathrm{CO_3}^{2-}} c_{\mathrm{CO_3}^{2-}}. \tag{6}$$

Driving force for precipitation

$$S = \frac{\gamma_{\mathrm{Ca}^{2+}} c_{\mathrm{Ca}^{2+}} \gamma_{\mathrm{CO_3}^{2-}} c_{\mathrm{CO_3}^{2-}}}{K_{sp}}. \tag{7}$$

Equilibrium equations

$$\xi_{i_1}^m C_{i_1}^m + \ldots + \xi_{i_Q}^m C_{i_Q}^m \leftrightarrow \xi_{j_1}^m C_{j_1}^m + \ldots + \xi_{j_Q}^k C_{j_Q}^m. \tag{8}$$

Ionic deposition equilibrium

$$\begin{aligned}
J^D_{\mathrm{Ca}^{2+}} - J^R_{\mathrm{CaCO_3}} - \sum_{m;A\in LHS(m)} \xi_A^m J_m^S + \sum_{m';A\in RHS(m')} \xi_A^{m'} J_{m'}^S &= 0 \\
J^D_{\mathrm{CO_3}^{2-}} - J^R_{\mathrm{CaCO_3}} - \sum_{m;B\in LHS(m)} \xi_B^m J_m^S + \sum_{m';B\in RHS(m')} \xi_B^{m'} J_{m'}^S &= 0 \\
J^D_{C_n} - \sum_{m;C_n\in LHS(m)} \xi_{C_n}^m J_m^S + \sum_{m';C_n\in RHS(m')} \xi_{C_n}^{m'} J_{m'}^S &= 0, \quad n \geq 3.
\end{aligned} \tag{9}$$

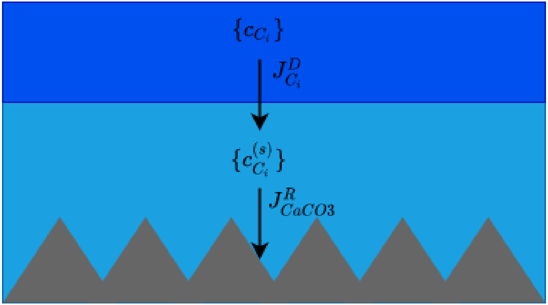


Figura: Schematic of the ionic deposition model.

$$\begin{bmatrix}\mathbf{I}_N & \mathbf{R} & \mathbf{S}\end{bmatrix}\begin{bmatrix}\mathbf{J}^D \\ J^R_{\mathrm{CaCO_3}} \\ \mathbf{J}^S\end{bmatrix} = \mathbf{0}, \tag{10}$$

$$\mathbf{R} = \begin{bmatrix}-1 \\ -1 \\ 0 \\ \vdots \\ 0\end{bmatrix} \quad \mathbf{S}_{n,m} = \begin{cases}-\xi^m_{C_n}, & C_n \in LHS(m) \\ \xi^m_{C_n}, & C_n \in RHS(m) \\ 0, \text{otherwise}\end{cases} . \tag{11}$$

Letting $\mathbf{V} := [\mathbf{v}_1 \ \ldots \ \mathbf{v}_{N-M}]$ basis of $\mathcal{N}(\mathbf{S}^T)$,

$$\mathbf{V}^T [\mathbf{I}_N \mathbf{R}] \begin{bmatrix}\mathbf{J}^D \\ J^R_{\mathrm{CaCO_3}}\end{bmatrix} = \mathbf{0}. \tag{12}$$

Chemical equilibrium closes the system.

Conservation of calcium (Ca) and carbon (C)

$$\sum_{i=1}^{N} \chi_i^{(\mathrm{Ca})} J_{C_i}^{D} = J_{\mathrm{CaCO_3}}^{R}$$
$$\sum_{i=1}^{N} \chi_i^{(\mathrm{C})} J_{C_i}^{D} = J_{\mathrm{CaCO_3}}^{R}; \quad (13)$$

conservation of every non-precipitating element E_j:

$$\sum_{i=1}^{N} \chi_i^{(E_j)} J_{C_i}^{D} = 0; \quad (14)$$

Conservation of electroneutrality

$$\sum_{i=1}^{N} z_i J_{C_i}^{D} = 0. \quad (15)$$

$$J^R_{\mathrm{CaCO_3}} = k_{r,d} K_{sp} (S_s - 1), \tag{16}$$

$$S_s = \frac{\gamma^{(s)}_{\mathrm{Ca}^{2+}} c^{(s)}_{\mathrm{Ca}^{2+}} \gamma^{(s)}_{\mathrm{CO_3}^{2-}} c^{(s)}_{\mathrm{CO_3}^{2-}}}{K_{sp}} \tag{17}$$

$$k_{r,d}(T) = k^{(0)}_{r,d} \exp\left(-\frac{E^{(0)}_{r,d}}{RT}\right), \tag{18}$$

$$D_T(y) = \frac{b_{\text{turb}}}{\text{Sc}_t}\frac{u_\star^3}{\nu^2}y^3, \tag{19}$$

$$\frac{\partial}{\partial y}\left((D_{C_i} + D_T(y))\frac{\partial c_{C_i}^{(i)}}{\partial y} \right) = 0, \tag{20}$$

$$J_{C_i}^D = (D_{C_i} + D_T(0))\frac{\partial c_{C_i}^{(i)}}{\partial y}\Big|_{y=0} = k_{i,d}(c_{C_i} - c_{C_i}^{(s)}), \tag{21}$$

$$k_{i,d} = \frac{3\sqrt{3}b_{\text{turb}}^{1/3}}{2\pi \text{Sc}_t^{1/3}}\left(\frac{D_{C_i}}{\nu}\right)^{2/3} u^\star, \tag{22}$$

For particle deposition, we consider that particles are deposited due to diffusion (turbulent diffusion and Brownian diffusion). We do *not* have a working model for turbophoresis at this moment.

$$\frac{\partial}{\partial y}\left(\left(D_{Br} + D_T(y+r)\right)\frac{\partial n_v}{\partial y}\right) = 0, \tag{23}$$

$$L_0(v) = \left(\int_0^\infty \frac{dy}{D_{Br} + D_T(y+r)}\right)^{-1}, \tag{24}$$

$$D_{Br} = \frac{k_b T}{6\pi\mu r}, \tag{25}$$

$$D_T(y) = \frac{b_{\text{turb}}}{Sc_t}\frac{u_\star^3}{\nu^2}y^3, \tag{26}$$

Considering hydrodynamic interaction and potential forces

$$v_\Phi(y) = -\frac{D_B}{k_b T}\frac{\partial \Phi}{\partial y}. \tag{27}$$

$$\frac{\partial}{\partial y}\left(\frac{D_B + D_T(y+r)}{G_d(y)}\frac{\partial n}{\partial y} - \frac{v_\Phi(y)}{G_d(y)} n\right) = 0. \tag{28}$$

$$L(v) = \left(\int_0^\infty \frac{G_d(y)}{D_B + D_T(y+r)} \exp\left(-\int_\infty^y \frac{v_\Phi(s)}{D_B + D_T(s+r)} ds\right) dy\right)^{-1} \tag{29}$$

We relate $L(v)$ and $L_0(v)$

$$L(v) = \frac{L_0(v)}{1 + (\omega_1 + \omega_2)L_0(v)}, \tag{30}$$

$$\omega_1 = -\int_0^{\delta_w} \frac{1}{D_B + D_T(y + r)} dy \tag{31}$$

$$\omega_2 = \int_0^{\delta_w} \frac{G_d(y)}{D_B + D_T(y + r)} \exp\left(\frac{1}{k_b T} \int_{\delta_w}^{y} \frac{\partial_s \Phi(s)}{1 + k_L(s + r)^3} ds\right) dy. \tag{32}$$

$$\delta_w = 5\frac{\nu}{u_\star} \tag{33}$$

Hydrodynamic potential

$$G_d(y) = 1 + \frac{r}{y} + 0.128\sqrt{\frac{r}{y}}, \tag{34}$$

Potential forces

$$\Phi(y) = \Phi_{VdW}(y) + \Phi_{DL}(y), \tag{35}$$

$$\Phi_{VdW}(y) = -\frac{H_A}{6}\left(\frac{2r(y+r)}{y(y+2r)} - \log\left(\frac{y+2r}{y}\right)\right) \tag{36}$$

$$\Phi_{DL}(y) = \epsilon_3 \Psi^2 r \log\left(1 + \exp\left(-\frac{y}{\lambda_D}\right)\right), \tag{37}$$

$$H = A \exp\left(-\frac{\Delta G^*}{k_b T}\right), \tag{38}$$

$$d^* = \frac{4 V_m \sigma_a}{k_b T \log S}. \tag{39}$$

$$\Delta G^* = \Delta G(d^*) = \frac{16}{3} \frac{\pi \sigma_a^3 V_m^3}{(k_b T \log S)^2}. \tag{40}$$

$$A = 2 \left(\frac{\pi}{6}\right)^{5/3} \frac{D}{V_m^{5/3}}. \tag{41}$$

$$D = \frac{k_b T}{3 \pi \mu d_*}. \tag{42}$$

$$G(v, c_{\mathrm{Ca}}) = J_{\mathrm{CaCO_3}} V_M \pi r^2. \tag{43}$$

$$J_{C_i}^D = \frac{D_{C_i}}{r}.(c_{C_i} - c_{C_i}^{(s)}) \tag{44}$$

$$J_{\mathrm{CaCO_3}} = \frac{k_{r,g}}{V_M}(\sqrt{S_s} - 1)^2. \tag{45}$$

$$B(v,w) = B_{Br}(v,w) + B_T(v,w) \tag{46}$$

$$B_{Br,0}(v,w) = \frac{2k_bT}{3\mu}\left(2 + \left(\frac{v}{w}\right)^{1/3} + \left(\frac{w}{v}\right)^{1/3}\right). \tag{47}$$

$$B_{Br}(v,w) = \frac{B_{Br,0}(v,w)}{W_{Br}(\hat{r})} \tag{48}$$

$$B_{T,0}(w,v) = c_{\text{turb}}\frac{3}{4\pi}\left(\frac{\epsilon_d}{\nu}\right)^{1/2}\left(v^{1/3} + w^{1/3}\right)^3, \tag{49}$$

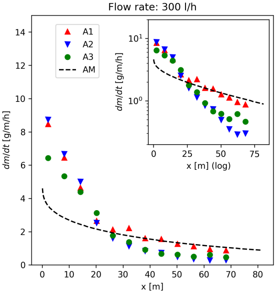
$$B_T(w,v) = \frac{B_{T,0}}{W_T(\hat{r})}\sigma\left(-2\frac{d_v}{\eta}\right)\sigma\left(-2\frac{d_w}{\eta}\right), \tag{50}$$

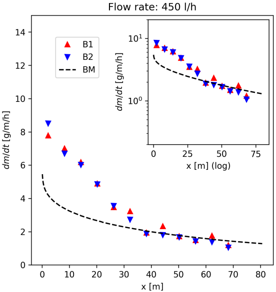
Pipe diameter	c^0_{Ca}	c^0_{Cl}	c^0_{Na}
11.2 mm	28 mM	56 mM	75 mM

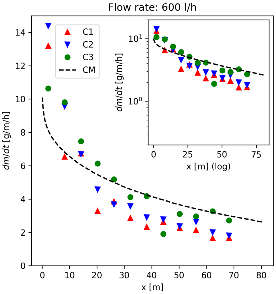
Tabela: Common conditions for all experiments element concentrations at the pipe inlet and pipe diameter.

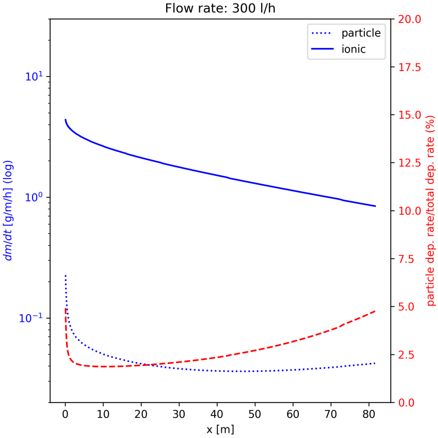
Tag	Fl. rate (l/h)	U (m/s)	pH tank Na	c_C (mM)	T (C)
A1	300	0.877	8.85	67.18	25.2
A2			8.88	66.73	25.2
A3			8.94	65.79	22.0
AM			-	66.57	24.2
B1	450	1.315	8.98	65.13	22.6
B2			9.00	64.79	22.6
BM			-	64.57	22.6
C1	600	1.754	8.42	71.97	25.3
C2			8.52	71.09	25.5
C3			8.47	71.55	25.2
CM			-	71.54	25.3

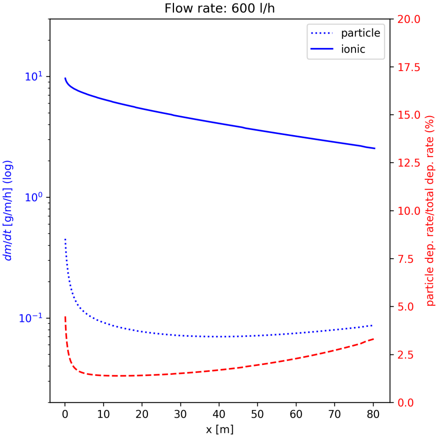
Tabela: Description of each experiment by differentiated initial conditions. Here, "M"stands for "model", and the numbered tags stands for experiments.

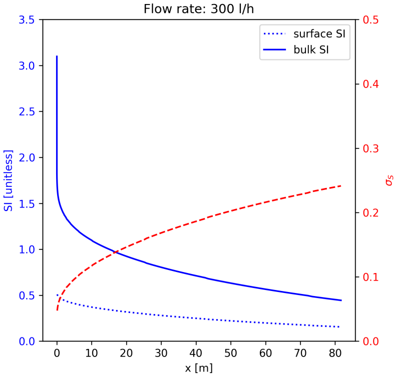

Flow rate: 300 l/h
A1
A2
A3
AM
dm/dt [g/m/h]
x [m]
0 10 20 30 40 50 60 70 80
0 2 4 6 8 10 12 14
10^1
10^0
0 25 50 75
x [m] (log)

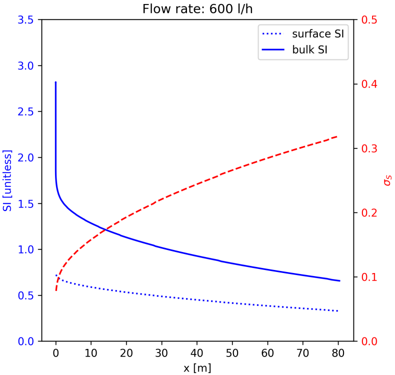

Flow rate: 450 l/h
B1
B2
BM
dm/dt [g/m/h]
x [m]
0 10 20 30 40 50 60 70 80
0 2 4 6 8 10 12 14
10^1
10^0
0 25 50 75
x [m] (log)

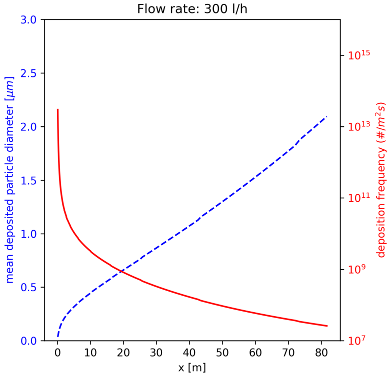

Flow rate: 600 l/h
C1
C2
C3
CM
dm/dt [g/m/h]
x [m]
0 10 20 30 40 50 60 70 80
0 2 4 6 8 10 12 14
10^1
10^0
0 25 50 75
x [m] (log)

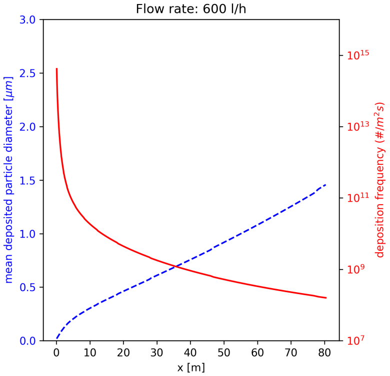

Flow rate: 300 l/h
particle
ionic
10^1
10^0
10^{-1}
dm/dt [g/m/h] (log)
particle dep. rate/total dep. rate (%)
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
0
10
20
30
40
50
60
70
80
x [m]

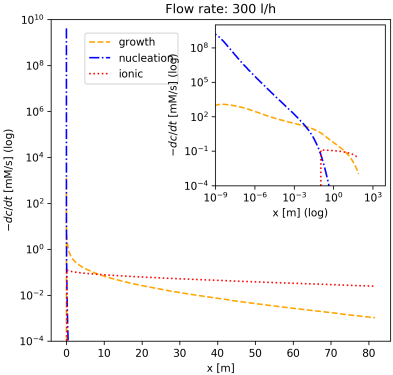

Flow rate: 600 l/h
particle
ionic
10^1
10^0
10^{-1}
dm/dt [g/m/h] (log)
particle dep. rate/total dep. rate (%)
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
0
10
20
30
40
50
60
70
80
x [m]

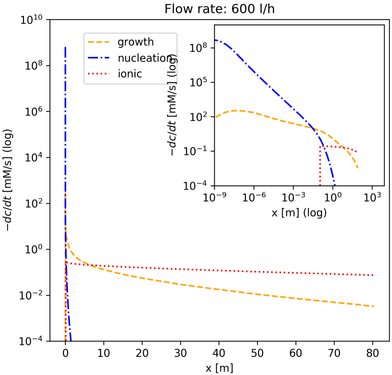

Flow rate: 300 l/h
surface SI
bulk SI
SI [unitless]
σ_S
x [m]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0.0
0.1
0.2
0.3
0.4
0.5
0
10
20
30
40
50
60
70
80

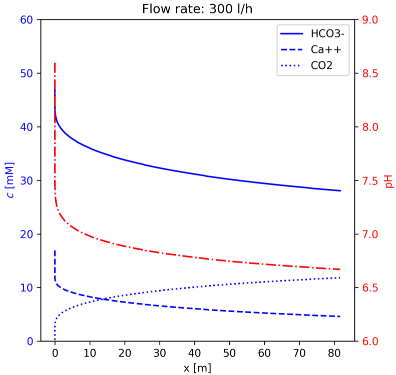

Flow rate: 600 l/h
surface SI
bulk SI
SI [unitless]
σ_S
x [m]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
0.0
0.1
0.2
0.3
0.4
0.5
0
10
20
30
40
50
60
70
80

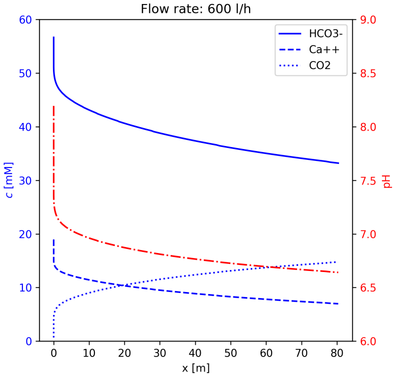

Flow rate: 300 l/h
mean deposited particle diameter [μm]
deposition frequency (#/m²s)
x [m]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
10⁷
10⁹
10¹¹
10¹³
10¹⁵
0
10
20
30
40
50
60
70
80


Flow rate: 600 l/h
mean deposited particle diameter [μm]
deposition frequency (#/m²s)
x [m]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
10⁷
10⁹
10¹¹
10¹³
10¹⁵
0
10
20
30
40
50
60
70
80


Flow rate: 300 l/h
growth
nucleation
ionic
−dc/dt [mM/s] (log)
x [m]
x [m] (log)


Flow rate: 600 l/h
growth
nucleation
ionic
−dc/dt [mM/s] (log)
x [m]
x [m] (log)


Flow rate: 300 l/h
c [mM]
pH
x [m]
HCO3-
Ca++
CO2
0
10
20
30
40
50
60
70
80
6.0
6.5
7.0
7.5
8.0
8.5
9.0

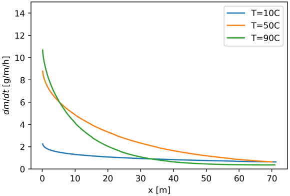

Flow rate: 600 l/h
c [mM]
pH
x [m]
HCO3-
Ca++
CO2
0
10
20
30
40
50
60
70
80
6.0
6.5
7.0
7.5
8.0
8.5
9.0

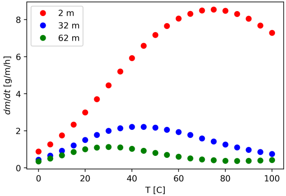
Pipe diameter	Flow velocity	c^0_{Cl}	c^0_{Na}
11.2 mm	0.877 m/s	56 mM	75 mM

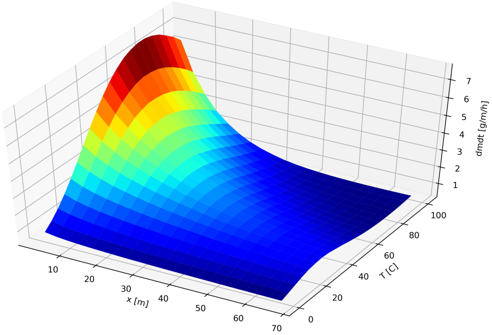
Tabela: Common parameters in all our explorations.

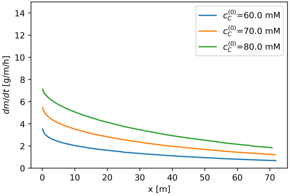
Temperature	c^0_{Ca}	c^0_{C}
25 $^\circ$ C	28 mM	68 mM

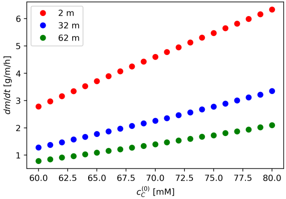
Tabela: Default parameters in our explorations, where variations are compared to.

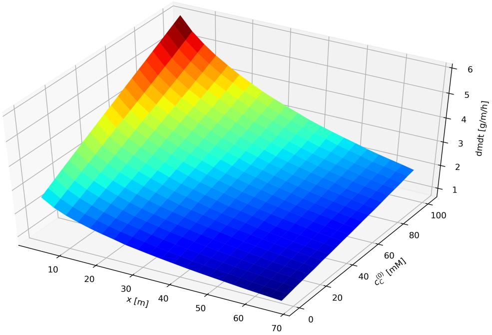

T=10C
T=50C
T=90C
dm/dt [g/m/h]
x [m]

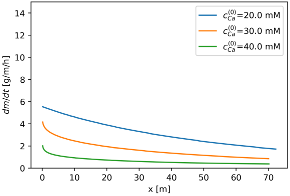

2 m
32 m
62 m
dm/dt [g/m/h]
T [C]

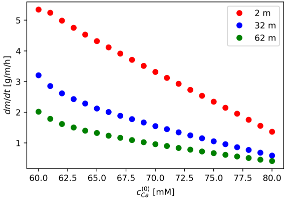

dmdt [g/m/h]
x [m]
T [C]

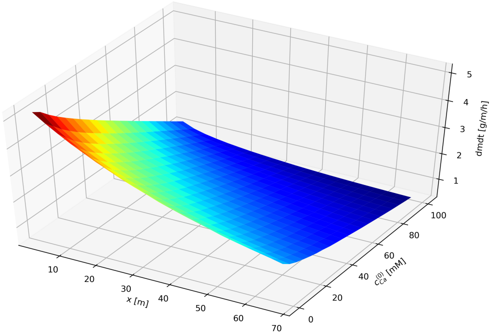

$c_C^{(0)}$=60.0 mM
$c_C^{(0)}$=70.0 mM
$c_C^{(0)}$=80.0 mM
dm/dt [g/m/h]
x [m]


2 m
32 m
62 m
dm/dt [g/m/h]
$c_C^{(0)}$ [mM]


dmdt [g/m/h]
x [m]
$c_C^{(0)}$ [mM]


$c_{Ca}^{(0)}$=20.0 mM
$c_{Ca}^{(0)}$=30.0 mM
$c_{Ca}^{(0)}$=40.0 mM
dm/dt [g/m/h]
x [m]


2 m
32 m
62 m
dm/dt [g/m/h]
$c_{Ca}^{(0)}$ [mM]


dmdt [g/m/h]
x [m]
$c_{Ca}^{(0)}$ [mM]