Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supporting Information:

A model-based technique for the determination of interfacial fluxes in gas-liquid flows in capillaries

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1 Derivation of the model equations

A mole balance of CO_2, using the bubble as control volume, can be used to find the relation between the change in bubble volume and the absorption rate of CO_2. In a reference frame travelling at a constant speed v_b along with the bubble, it holds that:

$$\frac{\mathrm{d}}{\mathrm{d}t}\Big(\frac{V_b(t)P(t)}{RT}\Big) = -NA_b \tag{S1}$$

with N the flux of CO_2 from the gas phase to the liquid phase for a single bubble and A_b the surface area of the bubble. This flux is usually expressed as [Levenspiel(1999)]:

$$N = \frac{1}{\left(\frac{k_G a}{H}\right)^{-1} + (k_L a E)^{-1}}\Big(\frac{P(t)}{H} - c(t)\Big) \tag{S2}$$

If it is assumed that the resistance to mass transfer in the gaseous phase ($H/k_G a$) is negligible, then expression (S2) can be simplified:

$$N = k_L a E\Big(\frac{P(t)}{H} - c_L(t)\Big) \tag{S3}$$

k_L represents the mass transfer coefficient in the liquid film, and a denotes the gas-liquid interfacial area per volume of contactor. For Taylor flow, this is equal to the interfacial area of a single bubble divided by the unit cell volume V_{uc}. E is the chemical enhancement factor, taking into account the increased mass transfer rate if rapid reactions take place in the liquid film surrounding the bubble. If no chemical reactions take place, E is simply equal to 1. $P(t)/H$ is the equilibrium concentration of the absorbed species in the liquid if Henry's law is assumed to be valid. H represents Henry's coefficient. Hence, $P(t)/H - c_L(t)$ represents the driving force for diffusion, where c_L stands for the bulk liquid concentration of the absorbent.

Solving equation (S1) for the rate of change of the bubble volume results in:

$$\frac{\mathrm{d}V_b(t)}{\mathrm{d}t} = -\frac{NaRTV_{uc}(t)}{P} - \frac{V_b(t)}{P(t)}\frac{\mathrm{d}P(t)}{\mathrm{d}t} \tag{S4}$$

If it is assumed that the majority of the liquid is trapped between two gas bubbles and the density of the liquid does not change appreciably whilst absorbing the gas, the liquid volume in a unit cell is given by the constant liquid slug volume. Under these assumptions, a change in the unit cell volume can be solely ascribed to a change in bubble volume, i.e.:

$$\frac{\mathrm{d}V_b(t)}{\mathrm{d}t} = \frac{\mathrm{d}V_{uc}(t)}{\mathrm{d}t} \tag{S5}$$

A mole balance of CO_2 using the liquid slug as a control volume is also required:

$$\frac{\mathrm{d}}{\mathrm{d}t}(V_s c(t)) = NaV_{uc}(t) - r(c)V_s \tag{S6}$$

with V_s the liquid slug volume and $r(c_L)$ the reaction rate per unit liquid slug volume. As previously mentioned, the liquid slug volume is assumed to be constant:

$$\frac{\mathrm{d}c(t)}{\mathrm{d}t} = Na\frac{V_{uc}(t)}{V_s} - r(c) \tag{S7}$$

Rapid absorption of a gaseous species also results in a significant bubble velocity change. For a stationary reference frame, a mole balance for CO_2 in the gas phase results in:

$$0 = (Au_G c_G)_x - (Au_G c_G)_{x+\Delta x} - NaA\Delta x \tag{S8}$$

$$\Rightarrow \frac{\mathrm{d}}{\mathrm{d}x}\frac{u_G P(x)}{RT} = -Na \tag{S9}$$

with u_G the superficial gas velocity, $c_G(x)$ the concentration of gas molecules in the bubble, x the axial coordinate, and A the cross-sectional area of the capillary. The superficial gas velocity u_G is related to the bubble velocity v_b by $u_G = \epsilon_G v_b$, with ϵ_G the gas void fraction.

Lastly, to calculate the pressure drop, a momentum balance is constructed using the unit cell as control volume in a reference frame moving along with the bubble. The rate of change of momentum can be ascribed to a pressure

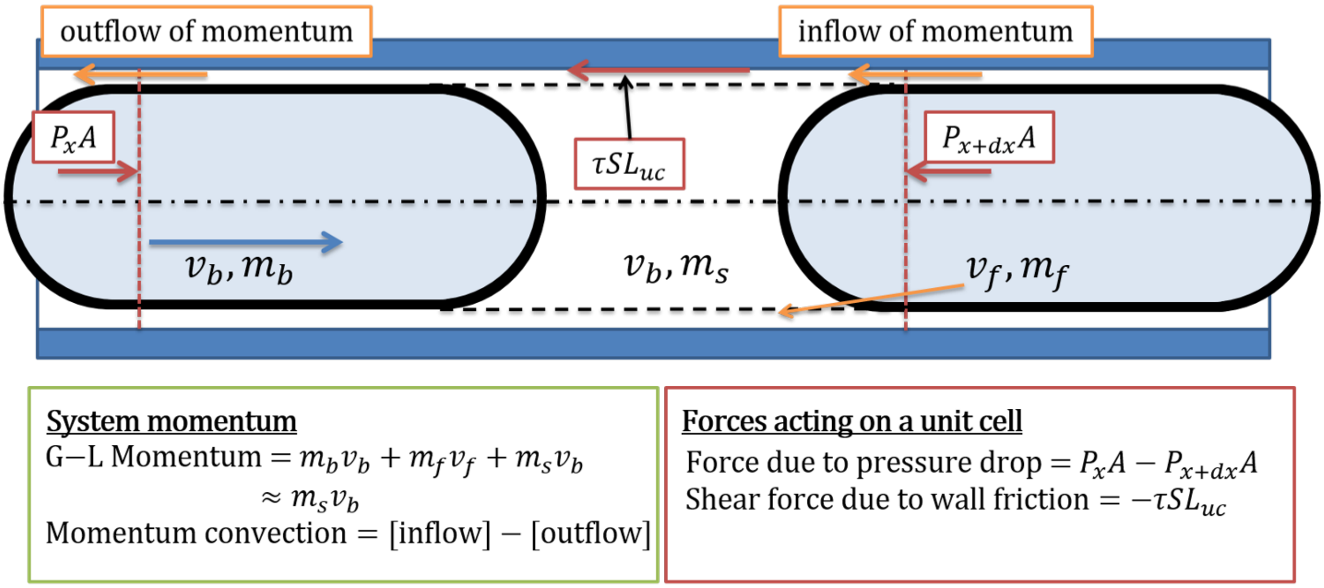


Figure S1: Illustration of the terms in the momentum balance

gradient across the unit cell, viscous and interfacial forces acting on the unit cell boundaries and the rate of momentum in- and outflow by convection:

$$\frac{\mathrm{d}m_s v_b(t)}{\mathrm{d}t} = -A\frac{\mathrm{d}P}{\mathrm{d}x}L_{uc} - \tau S L_{uc} + [\text{convection term}] \tag{S10}$$

With m_s the mass of the liquid slug, A the cross-sectional area of the capillary, S the cross-sectional perimeter, and L_{uc} the unit cell length. An illustration of the different contributions is provided in Figure S1. In deriving equation (S10), the following assumptions were made: (i) the mass of the liquid slug is much larger than the mass of the gas bubble and the mass of the liquid in the film between the bubble and the capillary wall, (ii) the slug velocity is equal to the bubble velocity, (iii) the interfacial forces and viscous forces can be lumped together in τ, (iv) the difference in pressure acting on both sides of the unit cell can be described by the local, averaged pressure gradient, and (v) the liquid film between the bubble and the capillary wall is thin and the velocity of the liquid inside this film is small. Hence, the rate of momentum in- and outflow by convection are assumed to be small and negligible. The pressure drop is given by:

$$\frac{\mathrm{d}P}{\mathrm{d}x} = -\rho_L \frac{\mathrm{d}v_b(t)}{\mathrm{d}t} - \frac{\tau S}{A} \tag{S11}$$

Rearranging equations (S4), (S5), (S9), (S7), and (S11), and making use of $\mathrm{d}x = v_b \mathrm{d}t$ results in the final model equations:

$$\frac{\mathrm{d}V_b}{\mathrm{d}x} = -\frac{NaV_{uc}}{v_b}\frac{RT}{P} - \frac{V_b}{P}\frac{\mathrm{d}P}{\mathrm{d}x} \tag{S12}$$

$$\frac{\mathrm{d}V_{uc}}{\mathrm{d}x} = -\frac{NaV_{uc}}{v_b}\frac{RT}{P} - \frac{V_b}{P}\frac{\mathrm{d}P}{\mathrm{d}x} \tag{S13}$$

$$\frac{\mathrm{d}v_b}{\mathrm{d}x} = -Na\frac{RT}{P} - \frac{\epsilon_G v_b}{P}\frac{\mathrm{d}P}{\mathrm{d}x} \tag{S14}$$

$$\frac{\mathrm{d}c}{\mathrm{d}x} = \frac{Na}{v_b}\frac{V_{uc}}{V_s} - \frac{r(c)}{v_b} \tag{S15}$$

$$\frac{\mathrm{d}P}{\mathrm{d}x} = \frac{\rho_L v_b Na\frac{RT}{P} - \frac{\tau S}{A}}{1 - \frac{\epsilon_G \rho_L v_b^2}{P}} \tag{S16}$$

1.1 Derivation of the quadratic program

Consider the optimality condition

$$\text{O.C.} = \int_{x_1}^{x_2} L\Big(v_b, \phi(x), \phi'(x), \dots\Big)\mathrm{d}x \tag{S17}$$

with

$$L = (v_b - v_b^{\mathrm{exp}})^2 + \Big(v_b - \frac{V_b^{\mathrm{exp}} + V_s}{C_1}\Big)^2 + \Big(v_b - \frac{V_{uc}^{\mathrm{exp}}}{C_1}\Big)^2 + \gamma\Big(\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\Big)^2 \tag{S18}$$

Assume that $\int$ can be approximated by $\sum$, so that for N experimental values of v_b:

$$\begin{aligned} \text{O.C.} \quad &= \quad \sum_{i=1}^{N}(v_{b,i} - v_{b,i}^{\mathrm{exp}})^2 + \Big(v_{b,i} - \frac{V_{b,i}^{\mathrm{exp}} + V_s}{C_1}\Big)^2 + \Big(v_{b,i} - \frac{V_{uc,i}^{\mathrm{exp}}}{C_1}\Big)^2 \\ &+ \quad \gamma \sum_{i=2}^{N-1} \psi_i^2 \end{aligned} \tag{S19}$$

with

$$\psi_i = \frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\bigg|_{\xi_i} \approx \frac{\phi_{i+1} + \phi_{i-1} - 2\phi_i}{(x_{i+1} - x_i)^2} \tag{S20}$$

Introduce three new dummy variables ξ, η and ζ such that

$$\xi_i = v_{b,i} - v_{b,i}^{\mathrm{exp}} \tag{S21}$$

$$\eta_i = v_{b,i} - \frac{V_{b,i}^{\mathrm{exp}} + V_s}{C_1} = \xi_i + v_{b,i}^{\mathrm{exp}} - \frac{V_{b,i}^{\mathrm{exp}} + V_s}{C_1} \tag{S22}$$

$$\zeta_i = v_{b,i} - \frac{V_{uc,i}^{\mathrm{exp}}}{C_1} = \xi_i + v_{b,i}^{\mathrm{exp}} - \frac{V_{uc,i}^{\mathrm{exp}}}{C_1} \tag{S23}$$

So that the constraint

$$\frac{V_s}{C_1}\Big(P_{k+1} - P_k\Big) = P_{k+1}v_{b,k+1} - P_k v_{b,k} + RT(x_{k+1} - x_k)\frac{\phi_{k+1} + \phi_k}{2} \tag{S24}$$

can be written as

$$P_{i+1}\xi_{b,i+1} - P_k\xi_{b,i} + RT(x_{i+1} - x_i)\frac{\phi_{i+1} + \phi_i}{2} = \frac{V_s}{C_1}\Big(P_{i+1} - P_i\Big) - P_{i+1}v_{b,i+1}^{\mathrm{exp}} + P_i v_{b,i}^{\mathrm{exp}} \tag{S25}$$

It can now be seen that, indeed, the optimal control problem reduces to a quadratic program:

$$\text{minimize} \quad : \quad \min_{\phi_i} \sum_{i=1}^{N}\Big(\xi_i^2 + \eta_i^2 + \zeta_i^2\Big) + \gamma \sum_{i=2}^{N-1} \psi_i \tag{S26}$$

$$\text{constraints} \quad : \quad \xi_{b,i+1}P_{i+1} - \xi_{b,i}P_i + \frac{RT}{2}(x_{i+1} - x_i)(\phi_{i+1} + \phi_i) = \frac{V_s}{C_1}\Big(P_{i+1} - P_i\Big) - P_{i+1}v_{b,i+1}^{\mathrm{exp}} + P_i v_{b,i}^{\mathrm{exp}} \tag{S27}$$

$$\eta_i - \xi_i = v_{b,i}^{\mathrm{exp}} - \frac{V_{b,i}^{\mathrm{exp}} + V_s}{C_1} \tag{S28}$$

$$\zeta_i - \xi_i = v_{b,i}^{\mathrm{exp}} - \frac{V_{uc,i}^{\mathrm{exp}}}{C_1} \tag{S29}$$

$$(x_{i+1} - x_i)^2\psi_i - (\phi_{i+1} + \phi_{i-1} - 2\phi_i) = 0 \tag{S30}$$

Or more concise

$$\text{minimize} \quad : \quad \min_{\mathbf{x}} \mathbf{x}^T\mathbf{H}\mathbf{x} \tag{S31}$$

$$\text{constraints} \quad : \quad \mathbf{A}\mathbf{x} = \mathbf{b} \tag{S32}$$

With

$$\mathbf{x} = (\xi_1, \ldots, \xi_N, \eta_1, \ldots, \eta_N, \zeta_1, \ldots, \zeta_N, \psi_2, \ldots, \psi_{N-1}, \phi_1, \ldots, \phi_N)^T \tag{S33}$$

$$\mathbf{H} = \begin{bmatrix} \mathbf{I}_{N\times N} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{I}_{N\times N} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{I}_{N\times N} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \gamma\mathbf{I}_{N-2\times N-2} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{0} \end{bmatrix} \tag{S34}$$

with $\mathbf{I}_{K\times K'}$ a unity matrix with K rows and K' columns.

$$\begin{aligned}
\mathbf{A} &= \begin{bmatrix} \mathbf{A}_1 & \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{A}_2 \\ -\mathbf{I}_{N\times N} & \mathbf{I}_{N\times N} & \mathbf{0} & \mathbf{0} & \mathbf{0} \\ -\mathbf{I}_{N\times N} & \mathbf{0} & \mathbf{I}_{N\times N} & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & \mathbf{A}_3 & \mathbf{A}_4 \end{bmatrix} && \text{(S35)} \\
\mathbf{A}_1 &= \begin{bmatrix} -P_1 & P_2 & 0 & \dots & 0 & 0 \\ 0 & -P_2 & P_3 & \dots & 0 & 0 \\ 0 & 0 & -P_3 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & \dots & P_{N-1} & 0 \\ 0 & 0 & 0 & \dots & -P_{N-1} & P_N \end{bmatrix} && \text{(S36)} \\
\mathbf{A}_2 &= \frac{RT}{2}\begin{bmatrix} x_2-x_1 & x_2-x_1 & 0 & \dots & 0 & 0 \\ 0 & x_3-x_2 & x_3-x_2 & \dots & 0 & 0 \\ 0 & 0 & x_4-x_3 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & \dots & x_{N-1}-x_{N-2} & 0 \\ 0 & 0 & 0 & \dots & x_N-x_{N-1} & x_N-x_{N-1} \end{bmatrix} && \text{(S37)} \\
\mathbf{A}_3 &= (x_{i+1}-x_i)^2\mathbf{I}_{N-2\times N-2} && \text{(S38)} \\
\mathbf{A}_4 &= \begin{bmatrix} -1 & 2 & -1 & \dots & 0 & 0 \\ 0 & -1 & 2 & \dots & 0 & 0 \\ 0 & 0 & -1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \ddots & 0 & 0 \\ 0 & 0 & 0 & \dots & -1 & 0 \\ 0 & 0 & 0 & \dots & 2 & -1 \end{bmatrix} && \text{(S39)}
\end{aligned}$$

and

$$\begin{aligned}
\mathbf{b} = {} & [v_{b,1}^{\mathrm{exp}}P_1 - v_{b,2}^{\mathrm{exp}}P_2 + \frac{V_s}{C_1}\Big(P_2 - P_1\Big), \dots, v_{b,N-1}^{\mathrm{exp}}P_{N-1} - v_{b,N}^{\mathrm{exp}}P_N + \frac{V_s}{C_1}\Big(P_N - P_{N-1}\Big), && \text{(S40)} \\
& v_{b,1}^{\mathrm{exp}} - \frac{V_{b,1}^{\mathrm{exp}} + V_s}{C_1}, \dots, v_{b,N}^{\mathrm{exp}} - \frac{V_{b,N}^{\mathrm{exp}} + V_s}{C_1}, v_{b,1}^{\mathrm{exp}} - \frac{V_{uc,1}^{\mathrm{exp}}}{C_1}, \dots, v_{b,N}^{\mathrm{exp}} - \frac{V_{uc,N}^{\mathrm{exp}}}{C_1}, 0, \dots, 0]^T
\end{aligned}$$

2 Model and fitting results

2.1 Model validation

The model equations S12 to S16 predict linear relationships between bubble volume, unit cell volume and bubble velocity:

$$V_{uc} = C_1 v_b \tag{S41}$$

$$V_b = -V_s + C_1 v_b \tag{S42}$$

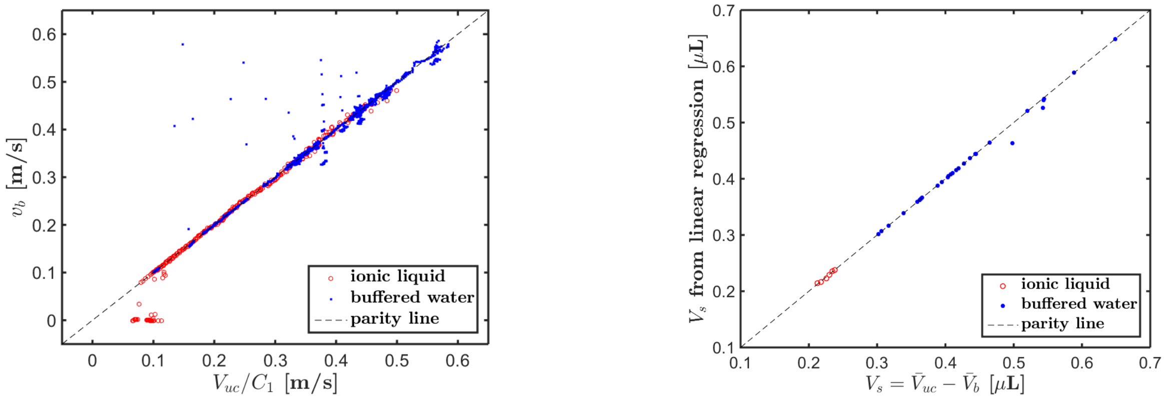
Eq. (S41) is confirmed by comparing V_{uc}/C_1 with v_b for CO_2 absorption in both the carbonate buffer (slow absorption) and ionic liquid (fast absorption). Figure S2a shows that almost all of the 1787 data points fall onto the parity line with only few outliers. Similarly, Figure S2b confirms Eq. (S42) by comparing V_s determined by (i) regressing V_b with v_b and (ii) by averaging $V_{uc} - V_b$ for both the carbonate buffer (slow absorpton) and ionic liquid (fast absorption).

2.2 The role of the fitting parameter γ

Figure S3 shows the behavior of the fitted volumetric flux Na as the smoothing parameter γ in expression

$$L = (v_b - v_b^{\mathrm{exp}})^2 + \Big(v_b - \frac{V_b^{\mathrm{exp}} + V_s}{C_1}\Big)^2 + \Big(v_b - \frac{V_{uc}^{\mathrm{exp}}}{C_1}\Big)^2 + \gamma\Big(\frac{\mathrm{d}^2\phi}{\mathrm{d}x^2}\Big)^2 \tag{S43}$$

increases. The influence of increasing γ can clearly be seen as the flux changes from wildly fluctuating to becoming insensitive to general trends. Note that for the special case of $\gamma = 0$, the fitting procedure is equal to direct substitution and differentiation of the experimental data in equations (S14).



(a) Linear correlation between unit cell volume and bubble velocity (equation (S41)).

(b) Equality between V_s determined using different methods.

Figure S2: Validation of the linear linear relationship between the unit cell volume and bubble velocity and the equality of slug volumes for different methods.

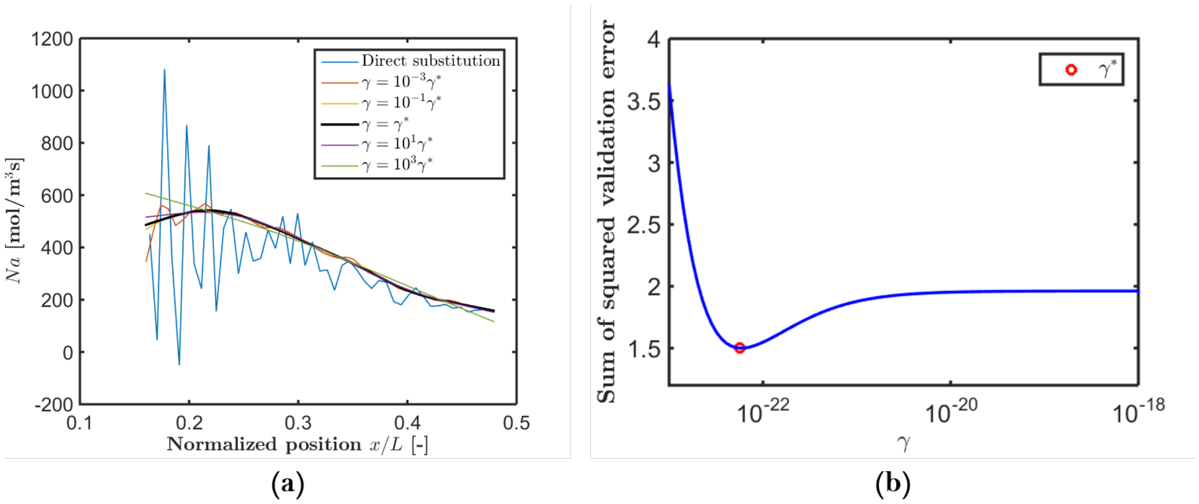


Figure S3: Influence of γ on (a) the fitted flux and (b) the resulting sum of squared validation error.

3 Scaling law relating the interfacial flux to the characteristic time

In the following we are assuming two limiting cases in which the absorption rate is independent of the hydrodynamic conditions. These are (i) an extremely fast reaction compared to the physical absorption process, so that the reaction proceeds very close to the gas-liquid interfacial area and (ii) a very slow reaction compared to the physical absorption process so that the liquid is essentially saturated, but a reaction in the bulk liquid keeps the absorption process going.

Case 1: For the very fast reaction with respect to the physical absorption, and assuming a first order reaction, one finds [Levenspiel(1999)]:

$$k_L E = \sqrt{k'''D} \tag{S44}$$

In this case, it is reasonable to assume that the bulk concentration is zero ($c = 0$), and hence the flux becomes:

$$N = \frac{\sqrt{k'''D}}{H} P \tag{S45}$$

Case 2: For a very slow reaction with respect to the physical absorption, the corresponding differential equation for the physically absorbed CO2 in a frame moving along with the bubble is (assuming a first order, irreversible reaction):

$$\frac{dc}{dt} = k_L a \left(\frac{P}{H} - c \right) - kc \tag{S46}$$

Assuming the system quickly reaches a pseudo steady state solution, the concentration is equal to:

$$c_{PSS} = \frac{k_L a}{k_L a + k} \frac{P}{H} \tag{S47}$$

And hence the flux is equal to (since the reaction is slow compared to the physical absorption $E \approx 1$):

$$N = k_L \left(1 - \frac{k_L a}{k_L a + k} \right) \frac{P}{H} = \frac{k_L k}{k_L a + k} \frac{P}{H} \tag{S48}$$

For the specific case of a very slow reaction ($k << k_L a$) this simplifies to

$$Na = \frac{k}{H} P \tag{S49}$$

In conclusion, in case 1 we find that the flux is proportional to the pressure and in case 2 we find the volumetric flux is proportional to the pressure. The pressure drop is given by Eqs. (24)–(27). However, for simplicity we assume the interfacial pressure drop term to be negligible. Note that these equations result in a HagenPoiseuille law with respect to the superficial liquid velocity:

$$P = P_{atm} + \frac{32\eta u_L}{d_c^2} (L - x) \tag{S50}$$

Hence, the average pressure in the observed capillary section is given by:

$$\overline{P} = P_{atm} + \frac{32\eta u_L}{d_c^2} \left(L - \frac{x_2 + x_1}{2} \right) \tag{S51}$$

For our data, there is a linear relationship between the characteristic time $t^* = (x_2 - x_1)/u_L$ and $u_L \left(L - \frac{x_2+x_1}{2} \right)$ (this is the experiment specific part of $\overline{P}$). This is shown in Figure S4. In our discussion, we will represent this symbolically as $u_L \left(L - \frac{x_2+x_1}{2} \right) = \alpha + \beta t^*$. Hence, the average flux changes linearly with the characteristic time:

$$\overline{N} = \frac{\sqrt{k'''D}}{H} \left[P_{atm} + \frac{32\eta}{d_c^2} (\alpha + \beta t^*) \right] \tag{S52}$$

or

$$\overline{Na} = \frac{k}{H} \left[P_{atm} + \frac{32\eta}{d_c^2} (\alpha + \beta t^*) \right] \tag{S53}$$

Note: α and β can be determined independently of $\overline{N}$ or $\overline{Na}$. Hence, the only fitting parameter remaining is the group $\sqrt{k'''D}/H$ or k/H. Fitting this equation to experimental data is more restrictive than fitting a generic straight line where both slope and intercept are varied independently. Least square fitting this factor to the

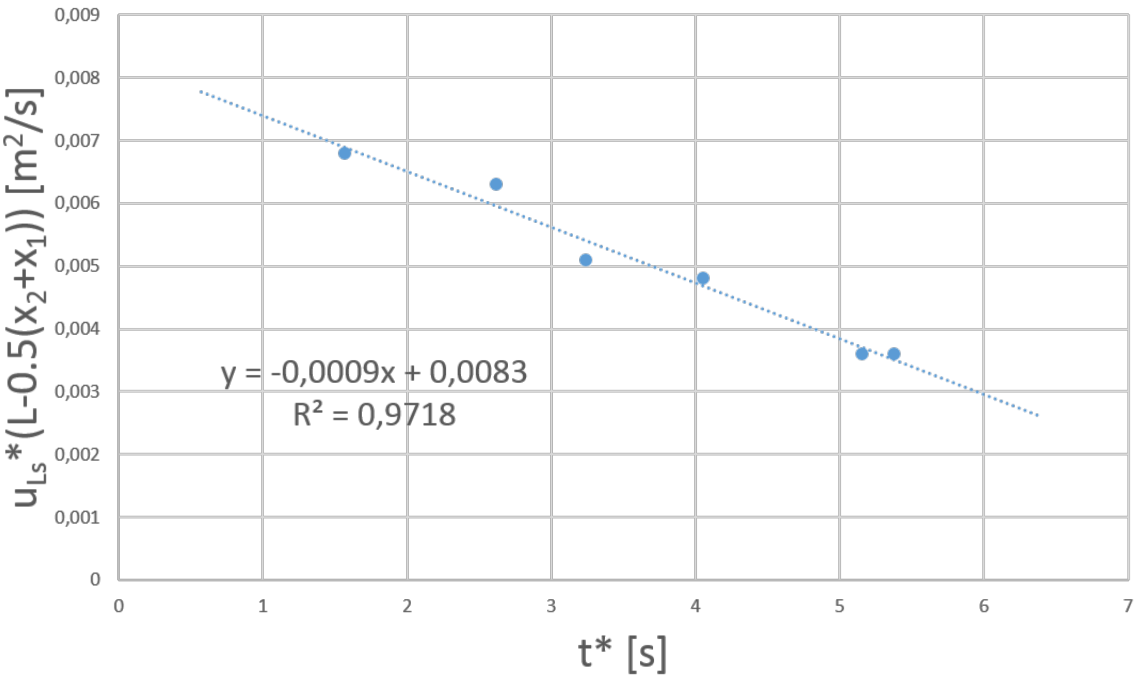


Figure S4: Linear relationship between the characteristic time $t^* = (x_2 - x_1)/u_L$ and $u_L \left(L - \frac{x_2+x_1}{2}\right)$.

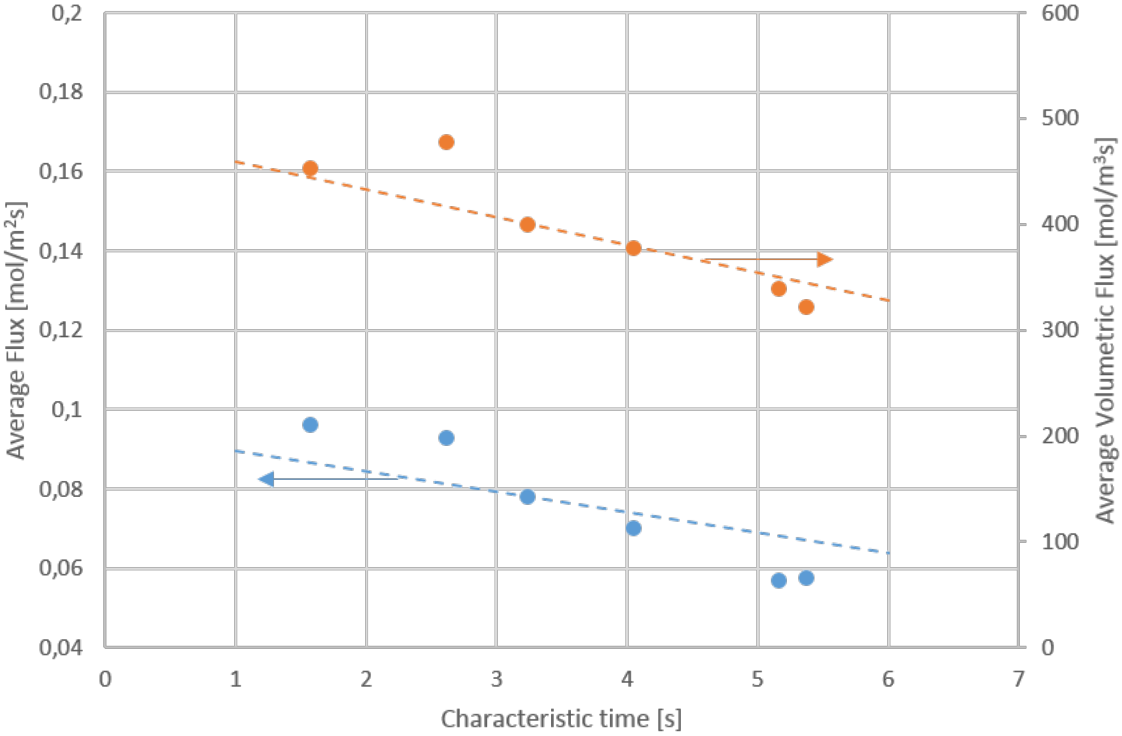


Figure S5: Fitted average fluxes versus the characteristic time.

experimental data gives $\sqrt{k'''D}/H = 4.67 \cdot 10^{-7}$ or $k/H = 0.0024$. The fitted curve for both cases is shown in Figure S5. The R^2 for the fast and slow case are resp. 0.668 and 0.775. It seems that in the case of a very slow reaction the slope is predicted more accurately compared to the case of a very fast reaction. If the second data point from the left for the volumetric flux is viewed as an outlier, k/H remains equal to 0.0024, but the R^2 improves to 0.936. None of the points for the fast case appear to be outliers and the general trend cannot be explained by the linear model with only one adjustable constant. It could be argued that the pre-factor of 32 in the pressure drop model is not realistic, however, in order to get a better fit, it has to be multiplied by a factor > 100. This is in our opinion very unrealistic and therefore we believe that the overall absorption rate (physical & chemical) is limited by the chemical reaction.

In summary, this result can be seen as the direct proportionality between the flux and driving force in case that the homogeneous reaction rate is slow compared to the mass transfer rate. As the characteristic time increases, the pressure in the capillary decreases, and hence the driving force decreases. Since the proportionality constant is unaffected by the changing hydrodynamic conditions, the relation between the driving force and the volumetric flux is directly observable. Although we suspect that ΔP and t^* are inversely proportional, the t^* range is too small to distinguish the goodness of the fit between $\Delta P = a + bt^*$ and $\Delta P = a' + b'/t^*$. Probably, because the latter expression can sufficiently be linearized in the studied t^* range. Nevertheless, directly plotting the flux versus the pressure drop clearly shows a linear relationship.

References

[Levenspiel(1999)] O. Levenspiel, *Chemical Reaction Engineering*, John Wiley & Sons, New York, 3rd edn, 1999, pp. 524–536.