

Supplementary Information
for
Kinetic Model for Moisture-Controlled CO₂
Sorptions

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A

Chemical reaction model section

A.1 Derivation of a_1 and a_2

We start from the following two equations in an open system:

$$\frac{\partial \theta}{\partial t} = [A]k_d[\text{H}_2\text{O}]^n \{2K_{\text{eq}(\text{eff})}P_{\text{CO}_2}(1 - \theta) - (2\theta - 1)^2\} \quad (\text{S.A.1})$$

$$0 = [A]k_d[\text{H}_2\text{O}]^n \{2K_{\text{eq}(\text{eff})}P_{\text{CO}_2(\text{eq})}(1 - \theta_{\text{eq}}) - (2\theta_{\text{eq}} - 1)^2\} \quad (\text{S.A.2})$$

Note that $P_{\text{CO}_2} = \text{const.} = P_{\text{CO}_2(\text{eq})}$ in an open system. The subtraction of these equations yields:

$$\frac{\partial \theta}{\partial t} = [A]k_d[\text{H}_2\text{O}]^n \left[(4 - 2K_{\text{eq}(\text{eff})}P_{\text{CO}_2})(\theta - \theta_{\text{eq}}) - 4(\theta^2 - \theta_{\text{eq}}^2) \right] \quad (\text{S.A.3})$$

$$= [A]k_d[\text{H}_2\text{O}]^n \left[-4\theta^2 + \theta(4 - 2K_{\text{eq}(\text{eff})}P_{\text{CO}_2}) + 4\theta_{\text{eq}}^2 - (4 - 2K_{\text{eq}(\text{eff})}P_{\text{CO}_2})\theta_{\text{eq}} \right] \quad (\text{S.A.4})$$

$$\equiv [A]k_d[\text{H}_2\text{O}]^n \left[a_1(\theta - \theta_{\text{eq}}) + a_2(\theta - \theta_{\text{eq}})^2 \right] \quad (\text{S.A.5})$$

$$= [A]k_d[\text{H}_2\text{O}]^n \left[a_2\theta^2 + \theta(a_1 - 2a_2\theta_{\text{eq}}) - a_1\theta_{\text{eq}} + a_2\theta_{\text{eq}}^2 \right] \quad (\text{S.A.6})$$

The comparison of the coefficients of the θ^0 , θ^1 and θ^2 terms yields:

$$a_2 = -4 \quad (\text{S.A.7})$$

$$a_1 - 2a_2\theta_{\text{eq}} = 4 - 2K_{\text{eq}(\text{eff})}P_{\text{CO}_2} \quad (\text{S.A.8})$$

$$-a_1\theta_{\text{eq}} + a_2\theta_{\text{eq}}^2 = 4\theta_{\text{eq}}^2 - (4 - 2K_{\text{eq}(\text{eff})}P_{\text{CO}_2})\theta_{\text{eq}} \quad (\text{S.A.9})$$

The value of a_2 is expressed by Eq.(S.A.7). a_1 can be derived by substituting Eq.(S.A.7) into Eq.(S.A.8) as:

$$a_1 = 4 - 2K_{\text{eq}(\text{eff})}P_{\text{CO}_2} - 8\theta_{\text{eq}} \quad (\text{S.A.10})$$

We have obtained a_1 and a_2 without using Eq.(S.A.9). One can confirm that Eq.(S.A.9) is automatically satisfied by substituting Eq.(S.A.7) and Eq.(S.A.10) into Eq.(S.A.9). Solving the isotherm equation for $K_{\text{eq}(\text{eff})}P_{\text{CO}_2}$ results in

$$K_{\text{eq}(\text{eff})}P_{\text{CO}_2} = \frac{(2\theta_{\text{eq}} - 1)^2}{2(1 - \theta_{\text{eq}})} \quad (\text{S.A.11})$$

Substituting this equation into Eq.(S.A.10) yields:

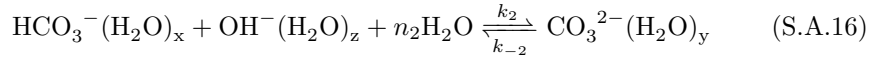
$$a_1 = 4 - 2 \frac{(2\theta_{\text{eq}} - 1)^2}{2(1 - \theta_{\text{eq}})} - 8\theta_{\text{eq}} \quad (\text{S.A.12})$$

$$= - \frac{(2\theta_{\text{eq}} - 1)(3 - 2\theta_{\text{eq}})}{1 - \theta_{\text{eq}}} \quad (\text{S.A.13})$$

This expression indicates that a_1 always takes a negative value in our Area of Interest ($0.5 < \theta_{\text{eq}} < 1$).

A.2 Derivation of the rate laws

We assume that the following three chemical reactions are elementary reactions:



We derive the rate laws in the following three possible cases, respectively.

Case I: The 1st reaction is the rate determining step

If the 1st reaction (Eq.(S.A.14)) is the slowest and the rate determining step, the 2nd and the 3rd reactions are in quasi-equilibrium, namely,

$$\frac{[\text{HCO}_3^-(\text{H}_2\text{O})_x][\text{H}_2\text{O}]^{n_1}}{[\text{CO}_{2(\text{aq})}][\text{OH}^-(\text{H}_2\text{O})_z]} \sim K_1 \quad (\text{S.A.17})$$

$$\frac{[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]}{[\text{HCO}_3^-(\text{H}_2\text{O})_x][\text{OH}^-(\text{H}_2\text{O})_z][\text{H}_2\text{O}]^{n_2}} \sim K_2 \quad (\text{S.A.18})$$

Substituting these equations into the 1st reaction yields:

$$\frac{\partial[\text{DIC}]}{\partial t} = -\frac{\partial[\text{CO}_{2(\text{g})}]}{\partial t} \quad (\text{S.A.19})$$

$$= k_H P_{\text{CO}_2} - k_{-H} [\text{CO}_{2(\text{aq})}] \quad (\text{S.A.20})$$

$$= k_H P_{\text{CO}_2} - k_{-H} \frac{[\text{HCO}_3^-(\text{H}_2\text{O})_x][\text{H}_2\text{O}]^{n_1}}{K_1[\text{OH}^-(\text{H}_2\text{O})_z]} \quad (\text{S.A.21})$$

$$= k_H P_{\text{CO}_2} - k_{-H} \frac{K_2[\text{HCO}_3^-(\text{H}_2\text{O})_x]^2[\text{H}_2\text{O}]^n}{K_1[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]} \quad (\text{S.A.22})$$

$$= \frac{k_H}{[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]} \left\{ P_{\text{CO}_2} [\text{CO}_3^{2-}(\text{H}_2\text{O})_y] - \frac{K_2}{K_1 K_H} [\text{HCO}_3^-(\text{H}_2\text{O})_x]^2 [\text{H}_2\text{O}]^n \right\} \quad (\text{S.A.23})$$

$$= \frac{2[\text{A}]k_{-H}K_2[\text{H}_2\text{O}]^n}{K_1[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]} \left\{ K_{\text{eq}(\text{eff})} P_{\text{CO}_2} [\text{CO}_3^{2-}(\text{H}_2\text{O})_y] - \frac{[\text{HCO}_3^-(\text{H}_2\text{O})_x]^2}{2[\text{A}]} \right\} \quad (\text{S.A.24})$$

Eq.(S.A.23) indicates that the overall reaction rate constants in Case I can be expressed as:

$$k_{a(\text{Case I})} = \frac{k_H}{[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]} \quad (\text{S.A.25})$$

$$k_{d(\text{Case I})} = \frac{k_H}{[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]} \left(\frac{K_{2(\text{AEM})}}{K_{1(\text{AEM})}K_{H(\text{AEM})}} \right) \quad (\text{S.A.26})$$

We can rewrite Eq.(S.A.23) in terms of θ as:

$$\frac{\partial \theta}{\partial t} = \frac{[A]k_{-H}K_2[\text{H}_2\text{O}]^n}{K_1[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]} \left\{ \frac{2K_{\text{eq}(\text{eff})}P_{\text{CO}_2}[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]}{[A]} - \frac{[\text{HCO}_3^-(\text{H}_2\text{O})_x]^2}{[A]^2} \right\} \quad (\text{S.A.27})$$

$$= \frac{[A]k_{-H}K_2[\text{H}_2\text{O}]^n}{K_1[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]} \left\{ 2K_{\text{eq}(\text{eff})}P_{\text{CO}_2}(1-\theta) - (2\theta-1)^2 \right\} \quad (\text{S.A.28})$$

$$= \frac{[A]k_{-H}K_2[\text{H}_2\text{O}]^n}{K_1[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]} \left[a_1(\theta - \theta_{\text{eq}}) + a_2(\theta - \theta_{\text{eq}})^2 \right] \quad (\text{S.A.29})$$

Note that we have the additional factor of $1/[\text{CO}_3^{2-}(\text{H}_2\text{O})_y](=1/\{[A](1-\theta)\})$ in the derived rate law (Eq.(S.A.29)) and the overall reaction rate constants (Eq.(S.A.25) and Eq.(S.A.26)). A Taylor expansion of $\frac{1}{1-\theta}$ around $\theta \sim \theta_{\text{eq}}$ yields:

$$\frac{1}{1-\theta} = \frac{1}{1-\theta_{\text{eq}}} \frac{1}{\left(1 - \frac{\theta - \theta_{\text{eq}}}{1-\theta_{\text{eq}}}\right)} \quad (\text{S.A.30})$$

$$= \frac{1}{1-\theta_{\text{eq}}} \sum_{n=0}^{\infty} \left(\frac{\theta - \theta_{\text{eq}}}{1-\theta_{\text{eq}}} \right)^n \quad (\text{S.A.31})$$

Therefore, the additional factor of $1/[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]$ yields the higher order terms in the rate law.

Case II: The 2nd reaction is the rate determining step

If the 2nd reaction (Eq.(S.A.15)) is the slowest and the rate determining step, the 1st and the 3rd reactions are in quasi-equilibrium, namely,

$$\frac{[\text{CO}_2(\text{aq})]}{P_{\text{CO}_2}} \sim K_H \quad (\text{S.A.32})$$

$$\frac{[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]}{[\text{HCO}_3^-(\text{H}_2\text{O})_x][\text{OH}^-(\text{H}_2\text{O})_z][\text{H}_2\text{O}]^{n_2}} \sim K_2 \quad (\text{S.A.33})$$

Substituting these equations into the 2nd reaction yields:

$$\frac{\partial[\text{DIC}]}{\partial t} = -\frac{\partial[\text{CO}_{2(\text{aq})}]}{\partial t} \quad (\text{S.A.34})$$

$$= k_1[\text{CO}_{2(\text{aq})}][\text{OH}^-(\text{H}_2\text{O})_z] - k_{-1}[\text{HCO}_3^-(\text{H}_2\text{O})_x][\text{H}_2\text{O}]^{n_1} \quad (\text{S.A.35})$$

$$= k_1 K_H P_{\text{CO}_2} \frac{[\text{CO}_3^{2-}(\text{H}_2\text{O})_y]}{K_2[\text{HCO}_3^-(\text{H}_2\text{O})_x][\text{H}_2\text{O}]^{n_2}} - k_{-1}[\text{HCO}_3^-(\text{H}_2\text{O})_x][\text{H}_2\text{O}]^{n_1} \quad (\text{S.A.36})$$

$$= \frac{k_{-1}}{[\text{HCO}_3^-(\text{H}_2\text{O})_x]} \left\{ \frac{K_1 K_H}{K_2 [\text{H}_2\text{O}]^{n_2}} P_{\text{CO}_2} [\text{CO}_3^{2-}(\text{H}_2\text{O})_y] - [\text{HCO}_3^-(\text{H}_2\text{O})_x]^2 [\text{H}_2\text{O}]^{n_1} \right\} \quad (\text{S.A.37})$$

$$= \frac{k_{-1}}{[\text{HCO}_3^-(\text{H}_2\text{O})_x]} \frac{K_1 K_H}{K_2 [\text{H}_2\text{O}]^{n_2}} \left\{ P_{\text{CO}_2} [\text{CO}_3^{2-}(\text{H}_2\text{O})_y] - \frac{K_2}{K_1 K_H} [\text{HCO}_3^-(\text{H}_2\text{O})_x]^2 [\text{H}_2\text{O}]^{n_1} \right\} \quad (\text{S.A.38})$$

$$= \frac{2[\text{A}]k_{-1}[\text{H}_2\text{O}]^{n_1}}{[\text{HCO}_3^-(\text{H}_2\text{O})_x]} \left\{ K_{\text{eq}(\text{eff})} P_{\text{CO}_2} [\text{CO}_3^{2-}(\text{H}_2\text{O})_y] - \frac{[\text{HCO}_3^-(\text{H}_2\text{O})_x]^2}{2[\text{A}]} \right\} \quad (\text{S.A.39})$$

Eq.(S.A.38) indicates that the overall reaction rate constants in Case II can be expressed as:

$$k_{a(\text{Case II})} = \frac{k_{-1}[\text{H}_2\text{O}]^{-n_2}}{[\text{HCO}_3^-(\text{H}_2\text{O})_x]} \left(\frac{K_{1(\text{AEM})} K_{H(\text{AEM})}}{K_{2(\text{AEM})}} \right) \quad (\text{S.A.40})$$

$$k_{d(\text{Case II})} = \frac{k_{-1}[\text{H}_2\text{O}]^{-n_2}}{[\text{HCO}_3^-(\text{H}_2\text{O})_x]} \quad (\text{S.A.41})$$

We can rewrite Eq.(S.A.38) in terms of θ as:

$$\frac{\partial\theta}{\partial t} = \frac{[\text{A}]k_{-1}[\text{H}_2\text{O}]^{n_1}}{[\text{HCO}_3^-(\text{H}_2\text{O})_x]} \left\{ \frac{2K_{\text{eq}(\text{eff})} P_{\text{CO}_2} [\text{CO}_3^{2-}(\text{H}_2\text{O})_y]}{[\text{A}]} - \frac{[\text{HCO}_3^-(\text{H}_2\text{O})_x]^2}{[\text{A}]^2} \right\} \quad (\text{S.A.42})$$

$$= \frac{[\text{A}]k_{-1}[\text{H}_2\text{O}]^{n_1}}{[\text{HCO}_3^-(\text{H}_2\text{O})_x]} \left\{ 2K_{\text{eq}(\text{eff})} P_{\text{CO}_2} (1 - \theta) - (2\theta - 1)^2 \right\} \quad (\text{S.A.43})$$

$$= \frac{[\text{A}]k_{-1}[\text{H}_2\text{O}]^{n_1}}{[\text{HCO}_3^-(\text{H}_2\text{O})_x]} \left[a_1(\theta - \theta_{\text{eq}}) + a_2(\theta - \theta_{\text{eq}})^2 \right] \quad (\text{S.A.44})$$

Note that we have the additional factor of $1/[\text{HCO}_3^-(\text{H}_2\text{O})_x]$ ($= 1/\{[\text{A}](2\theta - 1)\}$) in the derived rate law (Eq.(S.A.44)) and the overall reaction rate constants (Eq.(S.A.40) and Eq.(S.A.41)). A Taylor expansion of $\frac{1}{2\theta - 1}$ around $\theta \sim \theta_{\text{eq}}$ yields:

$$\frac{1}{2\theta - 1} = \frac{1}{2(\theta_{\text{eq}} - 0.5)} \frac{1}{\left(1 - \frac{\theta - \theta_{\text{eq}}}{0.5 - \theta_{\text{eq}}}\right)} \quad (\text{S.A.45})$$

$$= \frac{1}{2(\theta_{\text{eq}} - 0.5)} \sum_{n=0}^{\infty} \left(\frac{\theta - \theta_{\text{eq}}}{0.5 - \theta_{\text{eq}}}\right)^n \quad (\text{S.A.46})$$

Therefore, the additional factor of $1/[\text{HCO}_3^-]$ yields the higher order terms in the rate law.

Case III: The 3rd reaction is the rate determining step

If the 3rd reaction (Eq.(S.A.16)) is the slowest and the rate determining step, the 1st and the 2nd reactions are in quasi-equilibrium, namely,

$$\frac{[\text{CO}_{2(\text{aq})}]}{P_{\text{CO}_2}} \sim K_H \quad (\text{S.A.47})$$

$$\frac{[\text{HCO}_3^- (\text{H}_2\text{O})_x][\text{H}_2\text{O}]^{n_1}}{[\text{CO}_{2(\text{aq})}][\text{OH}^- (\text{H}_2\text{O})_z]} \sim K_1 \quad (\text{S.A.48})$$

Substituting these equations into the 3rd reaction yields:

$$\frac{\partial[\text{DIC}]}{\partial t} = -\frac{\partial[\text{CO}_3^{2-} (\text{H}_2\text{O})_y]}{\partial t} \quad (\text{S.A.49})$$

$$= -k_2[\text{HCO}_3^- (\text{H}_2\text{O})_x][\text{OH}^- (\text{H}_2\text{O})_z][\text{H}_2\text{O}]^{n_2} + k_{-2}[\text{CO}_3^{2-} (\text{H}_2\text{O})_y] \quad (\text{S.A.50})$$

$$= -k_2[\text{HCO}_3^- (\text{H}_2\text{O})_x] \frac{[\text{HCO}_3^- (\text{H}_2\text{O})_x][\text{H}_2\text{O}]^n}{K_H K_1 P_{\text{CO}_2}} + k_{-2}[\text{CO}_3^{2-} (\text{H}_2\text{O})_y] \quad (\text{S.A.51})$$

$$= k_{-2} \left\{ [\text{CO}_3^{2-} (\text{H}_2\text{O})_y] - \frac{K_2 [\text{H}_2\text{O}]^n [\text{HCO}_3^- (\text{H}_2\text{O})_x]^2}{K_H K_1 P_{\text{CO}_2}} \right\} \quad (\text{S.A.52})$$

$$= \frac{k_{-2}}{P_{\text{CO}_2}} \left\{ P_{\text{CO}_2} [\text{CO}_3^{2-} (\text{H}_2\text{O})_y] - \frac{K_2}{K_H K_1} [\text{HCO}_3^- (\text{H}_2\text{O})_x]^2 [\text{H}_2\text{O}]^n \right\} \quad (\text{S.A.53})$$

$$= \frac{2[\text{A}]k_2[\text{H}_2\text{O}]^n}{K_H K_1 P_{\text{CO}_2}} \left\{ K_{\text{eq}(\text{eff})} P_{\text{CO}_2} [\text{CO}_3^{2-} (\text{H}_2\text{O})_y] - \frac{[\text{HCO}_3^- (\text{H}_2\text{O})_x]^2}{2[\text{A}]} \right\} \quad (\text{S.A.54})$$

Eq.(S.A.53) indicates that the overall reaction rate constants in Case III can be expressed as:

$$k_{a(\text{Case III})} = \frac{k_{-2}}{P_{\text{CO}_2}} \quad (\text{S.A.55})$$

$$k_{d(\text{Case III})} = \frac{k_{-2}}{P_{\text{CO}_2}} \left(\frac{K_{2(\text{AEM})}}{K_{1(\text{AEM})} K_{H(\text{AEM})}} \right) \quad (\text{S.A.56})$$

We can rewrite Eq.(S.A.53) in terms of θ as:

$$\frac{\partial \theta}{\partial t} = \frac{[\text{A}]k_2[\text{H}_2\text{O}]^n}{K_H K_1 P_{\text{CO}_2}} \left\{ \frac{2K_{\text{eq}(\text{eff})} P_{\text{CO}_2} [\text{CO}_3^{2-}(\text{H}_2\text{O})_y]}{[\text{A}]} - \frac{[\text{HCO}_3^-(\text{H}_2\text{O})_x]^2}{[\text{A}]^2} \right\} \quad (\text{S.A.57})$$

$$= \frac{[\text{A}]k_2[\text{H}_2\text{O}]^n}{K_H K_1 P_{\text{CO}_2}} \left\{ 2K_{\text{eq}(\text{eff})} P_{\text{CO}_2} (1 - \theta) - (2\theta - 1)^2 \right\} \quad (\text{S.A.58})$$

$$= \frac{[\text{A}]k_2[\text{H}_2\text{O}]^n}{K_H K_1 P_{\text{CO}_2}} \left[a_1(\theta - \theta_{\text{eq}}) + a_2(\theta - \theta_{\text{eq}})^2 \right] \quad (\text{S.A.59})$$

Note that we have the additional factor of $1/P_{\text{CO}_2}$ in the derived rate law (Eq.(S.A.59)) and the overall reaction rate constants (Eq.(S.A.55) and Eq.(S.A.56)).

A.3 Derivation of the kinetics equations for a closed system

We start from the following two equations:

$$\frac{\partial \theta}{\partial t} = [A]k_d[\text{H}_2\text{O}]^n \{2K_{\text{eq}(\text{eff})}P_{\text{CO}_2}(1 - \theta) - (2\theta - 1)^2\} \quad (\text{S.A.60})$$

$$0 = [A]k_d[\text{H}_2\text{O}]^n \{2K_{\text{eq}(\text{eff})}P_{\text{CO}_2(\text{eq})}(1 - \theta_{\text{eq}}) - (2\theta_{\text{eq}} - 1)^2\} \quad (\text{S.A.61})$$

Subtracting the latter equation from the former equation yields:

$$\begin{aligned} \frac{\partial \theta}{\partial t} &= [A]k_d[\text{H}_2\text{O}]^n \\ &\times \left[\theta^2(-4 + 2K_{\text{eq}(\text{eff})}P_{\text{AEM}}) + \theta \left\{ 4 - 2K_{\text{eq}(\text{eff})}(P^* + P_{\text{AEM}}) \right\} \right. \\ &\left. + \left\{ -1 + 2K_{\text{eq}(\text{eff})}P^* - 2K_{\text{eq}(\text{eff})}P_{\text{eq}}(1 - \theta_{\text{eq}}) + (2\theta_{\text{eq}} - 1)^2 \right\} \right] \end{aligned} \quad (\text{S.A.62})$$

Note that we introduced $P_{\text{CO}_2} = P^* - P_{\text{AEM}}^*\theta$. We compare Eq.(S.A.62) with the following form:

$$\frac{\partial \theta}{\partial t} = [A]k_d[\text{H}_2\text{O}]^n \left\{ a'_1(\theta - \theta_{\text{eq}}) + a'_2(\theta - \theta_{\text{eq}})^2 \right\} \quad (\text{S.A.63})$$

$$= [A]k_d[\text{H}_2\text{O}]^n \left\{ a'_2\theta^2 + \theta(a'_1 - 2a'_2\theta_{\text{eq}}) - a'_1\theta_{\text{eq}} + a'_2\theta_{\text{eq}}^2 \right\} \quad (\text{S.A.64})$$

In order to make the coefficients of the θ^2 , θ^1 and θ^0 terms in Eq.(S.A.62) and Eq.(S.A.64) equivalent, the following equations need to be satisfied:

$$a'_2 = 2K_{\text{eq}(\text{eff})}P_{\text{AEM}}^* - 4 \quad (\text{S.A.65})$$

$$a'_1 - 2a'_2\theta_{\text{eq}} = 4 - 2K_{\text{eq}(\text{eff})}(P^* + P_{\text{AEM}}^*) \quad (\text{S.A.66})$$

$$-a'_1\theta_{\text{eq}} + a'_2\theta_{\text{eq}}^2 = -1 + 2K_{\text{eq}(\text{eff})}P^* - 2K_{\text{eq}(\text{eff})}P_{\text{eq}}(1 - \theta_{\text{eq}}) + (2\theta_{\text{eq}} - 1)^2 \quad (\text{S.A.67})$$

Substituting Eq.(S.A.65) into Eq.(S.A.66) yields:

$$a'_1 = 2(2\theta_{\text{eq}} - 1)(K_{\text{eq}(\text{eff})}P_{\text{AEM}}^* - 2) - 2K_{\text{eq}(\text{eff})}P^* \quad (\text{S.A.68})$$

We have obtained a'_1 and a'_2 without using Eq.(S.A.67). One can confirm that Eq.(S.A.67) is automatically satisfied if Eq.(S.A.65) and Eq.(S.A.68) are substituted into Eq.(S.A.67).

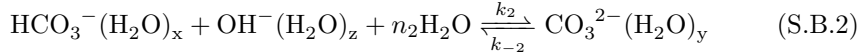
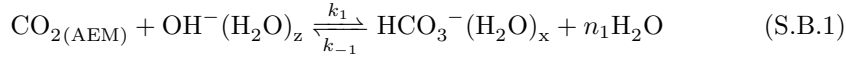
B

**Chemical reaction -
diffusion transport model
section**

B.1 Derivation of the non-linear diffusion equation for carbon transport

In this Chapter, we refer to HCO_3^- and CO_3^{2-} as C and D for convenience, respectively. C_i [mol/L], D_i [m²/s], z_i [non dim.] represents concentration, diffusivity and charge of each chemical species respectively. k_m and k_{-m} represents a forward or backward reaction rate constant of m -th chemical reaction respectively. Note that we ignore convection terms.

Now, we consider the following chemical reactions inside a sorbent:



where,

$$n_1 \equiv z - x \quad (\text{S.B.3})$$

$$n_2 \equiv y - 1 - x - z \quad (\text{S.B.4})$$

$$(\text{S.B.5})$$

x , y and z represent the hydration number of bicarbonate ions, carbonate ions and hydroxide ions, respectively. The time-dependent behavior of each chemical species' concentration in an anion exchange material can be described by the following Nernst-Planck time-dependent PDEs including diffusion terms ($-\vec{\nabla} \cdot (-D_i \vec{\nabla} C_i)$), chemical reaction terms ($S_{i_1} + S_{i_2} + \dots$) and migration current terms ($-\vec{\nabla} \cdot (z_i(C_i D_i) \vec{\mathcal{E}})$):

$$\frac{\partial C_i}{\partial t} = \underbrace{-\vec{\nabla} \cdot (-D_i \vec{\nabla} C_i)}_{\text{diffusion term}} + \underbrace{S_{i_1} + S_{i_2} + \dots + S_{i_N}}_{\text{chemical reaction kinetics term}} \underbrace{-\vec{\nabla} \cdot (z_i(C_i D_i) \vec{\mathcal{E}})}_{\text{migration term}} \quad (\text{S.B.6})$$

where,

$$\vec{\mathcal{E}} \equiv \frac{\sum_i z_i D_i \vec{\nabla} C_i}{\sum_i z_i^2 D_i C_i} \quad (\text{S.B.7})$$

S_{i_m} denotes a generated or consumed amount of the chemical species i in the m -th chemical reaction. We ignore only H^+ but take CO_2 and OH^- into consideration at first. The three PDEs that are relevant to DIC can be expressed as

$$\begin{aligned} \frac{\partial C_{\text{CO}_2}}{\partial t} &= \vec{\nabla} \cdot \left(D_{\text{CO}_2} \vec{\nabla} C_{\text{CO}_2} \right) \\ &\quad - k_1 C_{\text{CO}_2} C_{\text{OH}^-} + k_{-1} C_{\text{HCO}_3^-} C_{\text{H}_2\text{O}} \end{aligned} \quad (\text{S.B.8})$$

$$\begin{aligned} \frac{\partial C_{\text{HCO}_3^-}}{\partial t} &= \vec{\nabla} \cdot \left(D_{\text{HCO}_3^-} \vec{\nabla} C_{\text{HCO}_3^-} \right) \\ &\quad + \vec{\nabla} \cdot \left(C_{\text{HCO}_3^-} D_{\text{HCO}_3^-} \vec{\mathcal{E}} \right) \\ &\quad + k_1 C_{\text{CO}_2} C_{\text{OH}^-} - k_{-1} C_{\text{HCO}_3^-} C_{\text{H}_2\text{O}} \\ &\quad - k_2 C_{\text{HCO}_3^-} C_{\text{OH}^-} C_{\text{H}_2\text{O}} + k_{-2} C_{\text{CO}_3^{2-}} \end{aligned} \quad (\text{S.B.9})$$

$$\begin{aligned} \frac{\partial C_{\text{CO}_3^{2-}}}{\partial t} &= \vec{\nabla} \cdot \left(D_{\text{CO}_3^{2-}} \vec{\nabla} C_{\text{CO}_3^{2-}} \right) \\ &\quad + \vec{\nabla} \cdot \left(2C_{\text{CO}_3^{2-}} D_{\text{CO}_3^{2-}} \vec{\mathcal{E}} \right) \\ &\quad + k_2 C_{\text{HCO}_3^-} C_{\text{OH}^-} C_{\text{H}_2\text{O}} - k_{-2} C_{\text{CO}_3^{2-}} \end{aligned} \quad (\text{S.B.10})$$

where,

$$\vec{\mathcal{E}} = \frac{-D_{\text{OH}^-} \vec{\nabla} C_{\text{OH}^-} - D_{\text{HCO}_3^-} \vec{\nabla} C_{\text{HCO}_3^-} - 2D_{\text{CO}_3^{2-}} \vec{\nabla} C_{\text{CO}_3^{2-}} + D_{\text{H}^+} \vec{\nabla} C_{\text{H}^+}}{D_{\text{OH}^-} C_{\text{OH}^-} + D_{\text{HCO}_3^-} C_{\text{HCO}_3^-} + 4D_{\text{CO}_3^{2-}} C_{\text{CO}_3^{2-}} + D_{\text{H}^+} C_{\text{H}^+}} \quad (\text{S.B.11})$$

$$\sim \frac{-D_{\text{OH}^-} \vec{\nabla} C_{\text{OH}^-} - D_{\text{HCO}_3^-} \vec{\nabla} C_{\text{HCO}_3^-} - 2D_{\text{CO}_3^{2-}} \vec{\nabla} C_{\text{CO}_3^{2-}}}{D_{\text{OH}^-} C_{\text{OH}^-} + D_{\text{HCO}_3^-} C_{\text{HCO}_3^-} + 4D_{\text{CO}_3^{2-}} C_{\text{CO}_3^{2-}}} \quad (\text{S.B.12})$$

Now, we translate $C_{\text{HCO}_3^-}$ and $C_{\text{CO}_3^{2-}}$ into C_{OH^-} , [DICI] and [A] using charge neutrality:

$$C_{\text{HCO}_3^-} + 2C_{\text{CO}_3^{2-}} + C_{\text{OH}^-} = [\text{A}] + C_{\text{H}^+} \quad (\text{S.B.13})$$

$$\sim [\text{A}] \quad (\text{S.B.14})$$

Namely,

$$[\text{HCO}_3^-] = 2[\text{DICI}] + [\text{OH}^-] - [\text{A}] \quad (\text{S.B.15})$$

$$[\text{CO}_3^{2-}] = [\text{A}] - [\text{DICI}] - [\text{OH}^-] \quad (\text{S.B.16})$$

Substituting these two relations into the combined PDE obtained from Eq.(S.B.8), Eq.(S.B.9) and Eq.(S.B.10) yields:

$$\frac{\partial[\text{DIC}]}{\partial t} = -\vec{\nabla} \cdot (\vec{J}_{\text{DIC}(\text{diff})} + \vec{J}_{\text{DIC}(\text{mig})}) \quad (\text{S.B.17})$$

where,

$$\vec{J}_{\text{DIC}(\text{diff})} = -D_{\text{CO}_2} \vec{\nabla}[\text{CO}_2] - D_{\text{HCO}_3^-} \vec{\nabla}[\text{HCO}_3^-] - D_{\text{CO}_3^{2-}} \vec{\nabla}[\text{CO}_3^{2-}] \quad (\text{S.B.18})$$

$$\begin{aligned} &= -D_{\text{CO}_2} \vec{\nabla}[\text{CO}_2] \\ &\quad - D_{\text{HCO}_3^-} \vec{\nabla}(2[\text{DICl}] + [\text{OH}^-] - [\text{A}]) \\ &\quad - D_{\text{CO}_3^{2-}} \vec{\nabla}([\text{A}] - [\text{DICl}] - [\text{OH}^-]) \end{aligned} \quad (\text{S.B.19})$$

$$\begin{aligned} &= -D_{\text{CO}_2} \vec{\nabla}[\text{CO}_2] \\ &\quad - (2D_{\text{HCO}_3^-} - D_{\text{CO}_3^{2-}}) \vec{\nabla}[\text{DICl}] \\ &\quad - (D_{\text{HCO}_3^-} - D_{\text{CO}_3^{2-}}) \vec{\nabla}[\text{OH}^-] \end{aligned} \quad (\text{S.B.20})$$

$$\begin{aligned} &\vec{J}_{\text{DIC}(\text{mig})} \\ &= -(D_{\text{HCO}_3^-}[\text{HCO}_3^-] + 2D_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}]) \times \vec{\mathcal{E}} \end{aligned} \quad (\text{S.B.21})$$

$$\begin{aligned} &= \left[-2 \frac{[\text{DICl}]}{[\text{A}]} (D_{\text{HCO}_3^-} - D_{\text{CO}_3^{2-}}) - \frac{[\text{OH}^-]}{[\text{A}]} (D_{\text{HCO}_3^-} - 2D_{\text{CO}_3^{2-}}) + D_{\text{HCO}_3^-} - 2D_{\text{CO}_3^{2-}} \right] \\ &\quad \times \frac{(2D_{\text{CO}_3^{2-}} - D_{\text{HCO}_3^-} - D_{\text{OH}^-}) \vec{\nabla}[\text{OH}^-] + 2(D_{\text{CO}_3^{2-}} - D_{\text{HCO}_3^-}) \vec{\nabla}[\text{DICl}]}{\frac{[\text{DICl}]}{[\text{A}]} (2D_{\text{HCO}_3^-} - 4D_{\text{CO}_3^{2-}}) + \frac{[\text{OH}^-]}{[\text{A}]} (D_{\text{OH}^-} + D_{\text{HCO}_3^-} - 4D_{\text{CO}_3^{2-}}) - D_{\text{HCO}_3^-} + 4D_{\text{CO}_3^{2-}}} \end{aligned} \quad (\text{S.B.22})$$

When $[\text{CO}_2]$ and $[\text{OH}^-]$ can be regarded as negligible compared to $[\text{DIC}]$, the PDE simplifies to:

$$\begin{aligned}
[A] \frac{\partial \theta}{\partial t} &\sim \vec{\nabla} \cdot (D_C \vec{\nabla} C_C) + \vec{\nabla} \cdot (D_D \vec{\nabla} C_D) \\
&+ \vec{\nabla} \cdot \left((D_C C_C + 2D_D C_D) \times \underbrace{\frac{-D_C \vec{\nabla} C_C - 2D_D \vec{\nabla} C_D}{D_C C_C + 4D_D C_D}}_{=\vec{\varepsilon}} \right) \tag{S.B.23}
\end{aligned}$$

$$\begin{aligned}
&= [A] \vec{\nabla} \cdot ((2D_C - D_D) \vec{\nabla} \theta) \\
&+ [A] \vec{\nabla} \cdot \left(\{2\theta(D_C - D_D) - (D_C - 2D_D)\} \times \underbrace{\frac{-2(D_C - D_D) \vec{\nabla} \theta}{2\theta(D_C - 2D_D) - (D_C - 4D_D)}}_{=\vec{\varepsilon}} \right) \tag{S.B.24}
\end{aligned}$$

$$\begin{aligned}
&= [A] \vec{\nabla} \cdot ((2D_C - D_D) \vec{\nabla} \theta) \\
&+ [A] \vec{\nabla} \cdot \left(-2(D_C - D_D) \vec{\nabla} \theta \times \frac{2\theta(D_C - D_D) - (D_C - 2D_D)}{2\theta(D_C - 2D_D) - (D_C - 4D_D)} \right) \tag{S.B.25}
\end{aligned}$$

$$\begin{aligned}
&= [A] \vec{\nabla} \cdot \left[(\vec{\nabla} \theta) \left(\frac{1}{2\theta(D_C - 2D_D) - (D_C - 4D_D)} \right) \right. \\
&\quad \times \left. \left\{ 2\theta(2D_C - D_D)(D_C - 2D_D) - (2D_C - D_D)(D_C - 4D_D) \right. \right. \\
&\quad \left. \left. - 4\theta(D_C - D_D)^2 + 2(D_C - D_D)(D_C - 2D_D) \right\} \right] \tag{S.B.26}
\end{aligned}$$

$$= [A] \vec{\nabla} \cdot \left[(\vec{\nabla} \theta) \frac{D_C D_D (3 - 2\theta)}{2\theta(D_C - 2D_D) - (D_C - 4D_D)} \right] \tag{S.B.27}$$

$$\begin{aligned}
&= [A] \vec{\nabla} \cdot \left[(\vec{\nabla} \theta) \left(\frac{1}{2\theta(D_C - 2D_D) - (D_C - 4D_D)} \right) \right. \\
&\quad \times \left. \left\{ [2\theta(D_C - 2D_D) - (D_C - 4D_D)] \times \frac{-2D_C D_D}{2(D_C - 2D_D)} \right. \right. \\
&\quad \left. \left. - \frac{2(D_C - 4D_D)}{2(D_C - 2D_D)} D_C D_D + 3D_C D_D \right\} \right] \tag{S.B.28}
\end{aligned}$$

$$= [A] \vec{\nabla} \cdot \left[(\vec{\nabla} \theta) \left\{ \frac{-2D_C D_D}{2(D_C - 2D_D)} + \frac{-2(D_C - 4D_D) D_C D_D + 3D_C D_D}{2\theta(D_C - 2D_D) - (D_C - 4D_D)} \right\} \right] \tag{S.B.29}$$

$$= [A] \vec{\nabla} \cdot \left[(\vec{\nabla} \theta) D_C D_D \left\{ \frac{-1}{D_C - 2D_D} + \frac{\frac{4(D_C - D_D)}{2(D_C - 2D_D)}}{2\theta(D_C - 2D_D) - (D_C - 4D_D)} \right\} \right] \tag{S.B.30}$$

$$= [A] \vec{\nabla} \cdot \left[\left(\frac{D_C D_D}{D_C - 2D_D} \right) \left(-1 + \frac{2(D_C - D_D)}{2\theta(D_C - 2D_D) - (D_C - 4D_D)} \right) (\vec{\nabla} \theta) \right] \tag{S.B.31}$$

$$= -[A] \vec{\nabla} \cdot (-D_{\text{eff}} \vec{\nabla} \theta) \tag{S.B.32}$$

where,

$$D_{\text{eff}} \equiv \left(\frac{D_C D_D}{D_C - 2D_D} \right) \left(-1 + \frac{2(D_C - D_D)}{2\theta(D_C - 2D_D) - (D_C - 4D_D)} \right) \quad (\text{S.B.33})$$

We can confirm that the effective diffusivity (D_{eff}) satisfies the following relations:

$$D_{\text{eff}}(\theta = 0.5) = D_{\text{HCO}_3^-} \quad (\text{S.B.34})$$

$$D_{\text{eff}}(\theta = 1) = D_{\text{CO}_3^{2-}} \quad (\text{S.B.35})$$

These relations can be also confirmed in terms of diffusion flux and migration flux. The diffusion flux \vec{J}_{diff} can be expressed as:

$$\vec{J}_{\text{diff}} = -D_C \vec{\nabla} C_C - D_D \vec{\nabla} C_D \quad (\text{S.B.36})$$

$$= -(2D_C - D_D) \vec{\nabla} \theta \quad (\text{S.B.37})$$

Therefore, diffusion current \vec{I}_{diff} can be expressed as:

$$\vec{I}_{\text{diff}} = -F(2z_C D_C - z_D D_D) \vec{\nabla} \theta \quad (\text{S.B.38})$$

$$= 2F(D_C - D_D) \vec{\nabla} \theta \quad (\text{S.B.39})$$

On the other hand, $\vec{\mathcal{E}}$ can be written as:

$$\vec{\mathcal{E}} = \frac{2(D_D - D_C)}{D_C(2\theta - 1) + 4D_D(1 - \theta)} \vec{\nabla} \theta \quad (\text{S.B.40})$$

Therefore, migration flux \vec{J}_{mig} can be decomposed as:

$$\vec{J}_{\text{mig}} = \vec{J}_{\text{C(mig)}} + \vec{J}_{\text{D(mig)}} \quad (\text{S.B.41})$$

$$= Z_C D_C C_C \vec{\mathcal{E}} + Z_D D_D C_D \vec{\mathcal{E}} \quad (\text{S.B.42})$$

$$= -D_C C_C \frac{2(D_D - D_C)}{D_C(2\theta - 1) + 4D_D(1 - \theta)} \vec{\nabla} \theta - 2D_D C_D \frac{2(D_D - D_C)}{D_C(2\theta - 1) + 4D_D(1 - \theta)} \vec{\nabla} \theta \quad (\text{S.B.43})$$

$$= -D_C(2\theta - 1) \frac{2(D_D - D_C)}{D_C(2\theta - 1) + 4D_D(1 - \theta)} \vec{\nabla} \theta - 2D_D(1 - \theta) \frac{2(D_D - D_C)}{D_C(2\theta - 1) + 4D_D(1 - \theta)} \vec{\nabla} \theta \quad (\text{S.B.44})$$

Hence, migration current \vec{I}_{mig} can be expressed as

$$\vec{I}_{\text{mig}} = FZ_C \vec{J}_{C(\text{mig})} + FZ_D \vec{J}_{D(\text{mig})} \quad (\text{S.B.45})$$

$$\begin{aligned} &= FD_C(2\theta - 1) \frac{2(D_D - D_C)}{D_C(2\theta - 1) + 4FD_D(1 - \theta)} \vec{\nabla}\theta \\ &\quad + 4FD_D(1 - \theta) \frac{2(D_D - D_C)}{D_C(2\theta - 1) + 4FD_D(1 - \theta)} \vec{\nabla}\theta \quad (\text{S.B.46}) \end{aligned}$$

$$= 2F(D_D - D_C) \vec{\nabla}\theta \quad (\text{S.B.47})$$

$$= -\vec{I}_{\text{diff}} \quad (\text{S.B.48})$$

It confirms that the condition of null current is satisfied. We consider the two spacial cases: $\theta = 0.5$ and $\theta = 1$. Substituting these values into Eq.(S.B.37) and Eq.(S.B.44) yields:

$$\vec{J}_{\text{mig}}(\theta = 0.5) = \vec{J}_{D(\text{mig})}(\theta = 0.5) \quad (\text{S.B.49})$$

$$= (-D_D + D_C) \vec{\nabla}\theta \quad (\text{S.B.50})$$

$$\vec{J}_{\text{diff}}(\theta = 0.5) = (-2D_C + D_D) \vec{\nabla}\theta \quad (\text{S.B.51})$$

$$\vec{J}_{\text{mig}}(\theta = 1) = \vec{J}_{C(\text{mig})}(\theta = 1) \quad (\text{S.B.52})$$

$$= (-2D_D + 2D_C) \vec{\nabla}\theta \quad (\text{S.B.53})$$

$$\vec{J}_{\text{diff}}(\theta = 1) = (-2D_C + D_D) \vec{\nabla}\theta \quad (\text{S.B.54})$$

Thus,

$$\vec{J}_{\text{diff}} + \vec{J}_{\text{mig}} = \begin{cases} -D_C \vec{\nabla}\theta & (\text{if } \theta = 0.5) \\ -D_D \vec{\nabla}\theta & (\text{if } \theta = 1) \end{cases} \quad (\text{S.B.55})$$

Hence,

$$D_{\text{eff}} = \begin{cases} D_C & (\text{if } \theta = 0.5) \\ D_D & (\text{if } \theta = 1) \end{cases} \quad (\text{S.B.56})$$

B.2 Analytic solutions of a linear diffusion equation with a constant diffusivity for a flat sheet

We imagine that the normalized concentration of the sorbate per unit area, $\theta(x, t)$ ($0 < \theta < 1$). At time $t < 0$, the concentration inside a flat-sheet sorbent is uniformly distributed, i.e., $\theta(x, t < 0) = \theta_{\text{ini}}$. At $t = 0$, only the surface concentration suddenly changes from θ_{ini} to $\theta(x = 0, t) = \theta(x = L, t) = \theta_{\text{eq}}$. The time-development of the concentration $\theta(x, t)$ inside the flat sheet after $t > 0$ can be described by the following Partial Differential Equations (PDE) regarding the concentration $\theta(x, t)$, boundary conditions and an initial condition:

$$\frac{\partial \theta}{\partial t} = D \frac{\partial^2 \theta}{\partial x^2} \quad (\text{S.B.57})$$

$$\theta(0, t) = \theta_{\text{eq}} \quad (\text{S.B.58})$$

$$\theta(L, t) = \theta_{\text{eq}} \quad (\text{S.B.59})$$

$$\theta(x, 0) = P(x) \quad (\text{S.B.60})$$

where, L is the thickness of the flat sheet and D is the diffusivity of the sorbate inside the flat sheet. $P(x)$ is the initial distribution of the concentration defined as:

$$P(x) = \begin{cases} \theta_{\text{eq}} & (\text{if } x = 0, L) \\ \theta_{\text{ini}} & (\text{if } 0 < x < L) \end{cases} \quad (\text{S.B.61})$$

This is a homogeneous PDE with non-homogeneous boundary conditions. The steady state is obviously $\theta(x, t)|_{\text{steady}} = \theta(x, t = \infty) = \theta_{\text{eq}}$. So, if we define $\tilde{\theta}$ as

$$\theta(x, t) \equiv \tilde{\theta}(x, t) + \theta(x, t)|_{\text{steady}} \quad (\text{S.B.62})$$

$$= \tilde{\theta}(x, t) + \theta_{\text{eq}} \quad (\text{S.B.63})$$

then the system can be rewritten as

$$\frac{\partial \tilde{\theta}}{\partial t} = D \frac{\partial^2 \tilde{\theta}}{\partial x^2} \quad (\text{S.B.64})$$

$$\tilde{\theta}(0, t) = 0 \quad (\text{S.B.65})$$

$$\tilde{\theta}(L, t) = 0 \quad (\text{S.B.66})$$

$$\tilde{\theta}(x, 0) = \tilde{P}(x) \quad (\text{S.B.67})$$

$\tilde{P}(x)$ is the rewritten initial distribution of the concentration defined as:

$$\tilde{P}(x) = \begin{cases} 0 & (\text{if } x = 0, L) \\ -(\theta_{\text{eq}} - \theta_{\text{ini}}) & (\text{if } 0 < x < L) \end{cases} \quad (\text{S.B.68})$$

This rewritten system is a homogeneous PDE with homogeneous boundary conditions, so this system can be solved by the method of Separation of Variables. We define $h(t)$ and $\phi(x)$ as:

$$\tilde{\theta}(x, t) \equiv h(t)\phi(x) \quad (\text{S.B.69})$$

Then, we can define a constant number λ that is independent of both x and t as:

$$-\lambda \equiv \frac{1}{D} \frac{1}{h(t)} \frac{dh(t)}{dt} = \frac{1}{\phi(x)} \frac{d^2\phi(x)}{dx^2} \quad (\text{S.B.70})$$

We obtain the following two Ordinary Differential Equations (ODE):

$$\frac{d^2\phi(x)}{dx^2} = -\lambda\phi(x) \quad (\text{S.B.71})$$

$$\frac{dh(t)}{dt} = -\lambda Dh(t) \quad (\text{S.B.72})$$

We solve Eq.(S.B.71) first. In case of $\lambda = 0$, Eq.(S.B.71) reduces to

$$\frac{d^2\phi(x)}{dx^2} = 0 \quad (\text{S.B.73})$$

The general solutions can be expressed using some coefficients A and B as:

$$\phi(x) = Ax + B \quad (\text{S.B.74})$$

However, the boundary conditions demand $A = B = 0$, which results in a trivial solution.

In case of $\lambda > 0$, the general solutions of Eq.(S.B.71) are:

$$\phi(x) = A \sin(\sqrt{\lambda}x) + B \cos(\sqrt{\lambda}x) \quad (\text{S.B.75})$$

The boundary conditions demand:

$$Bh(t) = 0 \quad (\text{S.B.76})$$

$$(A \sin(\sqrt{\lambda}L) + B \cos(\sqrt{\lambda}L))h(t) = 0 \quad (\text{S.B.77})$$

Thus

$$B = 0 \quad (\text{S.B.78})$$

$$\lambda = \left(\frac{n\pi}{L}\right)^2 \quad (n = 1, 2, 3, \dots) \quad (\text{S.B.79})$$

Therefore we obtain multiple discrete solutions:

$$\phi_n(x) = a_n \sin\left(\frac{n\pi}{L}x\right) \quad (\text{S.B.80})$$

where, a_n is coefficients that need to be determined to satisfy the initial condition.

In case of $\lambda < 0$, the general solutions of Eq.(S.B.71) are:

$$\phi(x) = A \sinh(\sqrt{-\lambda}x) + B \cosh(\sqrt{-\lambda}x) \quad (\text{S.B.81})$$

The boundary conditions demand:

$$Bh(t) = 0 \quad (\text{S.B.82})$$

$$(A \sinh(\sqrt{-\lambda}L) + B \cosh(\sqrt{-\lambda}L))h(t) = 0 \quad (\text{S.B.83})$$

This results in $A = B = 0$, which indicates a trivial solution. After all, Eq.(S.B.80) is only the solutions for Eq.(S.B.71).

Next, we solve Eq.(S.B.72). Substituting Eq.(S.B.79) into Eq.(S.B.72) yields:

$$\frac{dh(t)}{dt} = -D \left(\frac{n\pi}{L}\right)^2 h(t) \quad (\text{S.B.84})$$

We obtain multiple discrete solutions for $h(t)$:

$$h_n(t) = Ae^{-D\left(\frac{n\pi}{L}\right)^2 t} \quad (n = 1, 2, 3, \dots) \quad (\text{S.B.85})$$

So, $\tilde{\theta}$ has the following multiple discrete solutions:

$$\tilde{\theta}_n(x, t) = a_n \sin\left(\frac{n\pi}{L}x\right) e^{-D\left(\frac{n\pi}{L}\right)^2 t} \quad (n = 1, 2, 3, \dots) \quad (\text{S.B.86})$$

So, the general solution can be expressed as:

$$\tilde{\theta}(x, t) = \sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi}{L}x\right) e^{-D\left(\frac{n\pi}{L}\right)^2 t} \quad (\text{S.B.87})$$

The initial condition demands:

$$\tilde{\theta}(x, t = 0) = \sum_{n=1}^{\infty} a_n \sin\left(\frac{n\pi}{L}x\right) \quad (\text{S.B.88})$$

$$= \tilde{P}(x) \quad (\text{S.B.89})$$

So,

$$\sum_{k=1}^{\infty} a_k \int_0^L \sin\left(\frac{k\pi}{L}x\right) \sin\left(\frac{n\pi}{L}x\right) dx = \int_0^L \tilde{P}(x) \sin\left(\frac{n\pi}{L}x\right) dx \quad (\text{S.B.90})$$

Note that:

$$\int_0^L \sin^2\left(\frac{n\pi}{L}x\right) dx = \int_0^L \frac{1 - \cos\left(\frac{2n\pi}{L}x\right)}{2} dx \quad (\text{S.B.91})$$

$$= \frac{L}{2} - \frac{1}{2} \int_0^L \cos\left(\frac{2n\pi}{L}x\right) dx \quad (\text{S.B.92})$$

$$= \frac{L}{2} - \frac{1}{2} \left(\frac{L}{2\pi n}\right) \left[\sin\left(\frac{2n\pi}{L}x\right)\right]_0^L \quad (\text{S.B.93})$$

$$= \frac{L}{2} \quad (\text{S.B.94})$$

and

$$\int_0^L \sin\left(\frac{k\pi}{L}x\right) \sin\left(\frac{n\pi}{L}x\right) dx = 0 \quad (\text{for } n \neq k) \quad (\text{S.B.95})$$

Thus

$$a_n = \frac{2}{L} \int_0^L \tilde{P}(x) \sin\left(\frac{n\pi}{L}x\right) dx \quad (\text{S.B.96})$$

$$= \frac{2}{L} (\theta_{\text{ini}} - \theta_{\text{eq}}) \int_0^L \sin\left(\frac{n\pi}{L}x\right) dx \quad (\text{S.B.97})$$

$$= -\frac{2}{L} (\theta_{\text{ini}} - \theta_{\text{eq}}) \left(\frac{L}{n\pi}\right) \left[\cos\left(\frac{n\pi}{L}x\right)\right]_0^L \quad (\text{S.B.98})$$

$$= \frac{2(\theta_{\text{eq}} - \theta_{\text{ini}})}{n\pi} \{(-1)^n - 1\} \quad (\text{S.B.99})$$

$$(\text{S.B.100})$$

Therefore

$$\tilde{\theta}(x, t) = \sum_{n=1}^{\infty} \frac{2(\theta_{\text{eq}} - \theta_{\text{ini}})}{n\pi} \{(-1)^n - 1\} \sin\left(\frac{n\pi}{L}x\right) e^{-D\left(\frac{n\pi}{L}\right)^2 t} \quad (\text{S.B.101})$$

$$\theta(x, t) = \theta_{\text{eq}} + \sum_{n=1}^{\infty} \frac{2(\theta_{\text{eq}} - \theta_{\text{ini}})}{n\pi} \{(-1)^n - 1\} \sin\left(\frac{n\pi}{L}x\right) e^{-D\left(\frac{n\pi}{L}\right)^2 t} \quad (\text{S.B.102})$$

We define the total saturation in a sorbent $\langle\theta\rangle$ as:

$$\langle\theta\rangle(t) \equiv \frac{1}{L} \int_0^L \theta(x, t) dx \quad (\text{S.B.103})$$

$$= \frac{1}{L} \int_0^L (\theta_{\text{eq}} + \tilde{\theta}(x, t)) dx \quad (\text{S.B.104})$$

$$= \theta_{\text{eq}} + \frac{1}{L} \int_0^L \tilde{\theta}(x, t) dx \quad (\text{S.B.105})$$

$$= \theta_{\text{eq}} + \frac{1}{L} \sum_{n=1}^{\infty} a_n \int_0^L \sin\left(\frac{n\pi}{L}x\right) e^{-D\left(\frac{n\pi}{L}\right)^2 t} dx \quad (\text{S.B.106})$$

$$= \theta_{\text{eq}} - \frac{1}{L} \sum_{n=1}^{\infty} a_n \left[\left(\frac{L}{n\pi}\right) \cos\left(\frac{n\pi}{L}x\right) e^{-D\left(\frac{n\pi}{L}\right)^2 t} \right]_0^L \quad (\text{S.B.107})$$

$$= \theta_{\text{eq}} - \sum_{n=1}^{\infty} a_n \left(\frac{1}{n\pi}\right) \{(-1)^n - 1\} e^{-D\left(\frac{n\pi}{L}\right)^2 t} \quad (\text{S.B.108})$$

$$= \theta_{\text{eq}} - \sum_{n=1}^{\infty} \frac{2(\theta_{\text{eq}} - \theta_{\text{ini}})}{(n\pi)^2} \{(-1)^n - 1\}^2 e^{-D\left(\frac{n\pi}{L}\right)^2 t} \quad (\text{S.B.109})$$

$$= \theta_{\text{eq}} - 8(\theta_{\text{eq}} - \theta_{\text{ini}}) \times \left[\frac{1}{1 \cdot \pi^2} e^{-D\left(\frac{1\pi}{L}\right)^2 t} + \frac{1}{9 \cdot \pi^2} e^{-D\left(\frac{3\pi}{L}\right)^2 t} + \frac{1}{25 \cdot \pi^2} e^{-D\left(\frac{5\pi}{L}\right)^2 t} + \dots \right] \quad (\text{S.B.110})$$

Therefore,

$$\frac{\langle\theta\rangle - \theta_{\text{eq}}}{\theta_{\text{ini}} - \theta_{\text{eq}}} = 8 \times \left[\frac{1}{1 \cdot \pi^2} e^{-D\left(\frac{1\pi}{L}\right)^2 t} + \frac{1}{9 \cdot \pi^2} e^{-D\left(\frac{3\pi}{L}\right)^2 t} + \frac{1}{25 \cdot \pi^2} e^{-D\left(\frac{5\pi}{L}\right)^2 t} + \dots \right] \quad (\text{S.B.111})$$

Fig.(B.1) and Fig.(B.2) compare the 1st term of Eq.(S.B.111) and the summation including higher order terms, assuming $D = 7 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and $L = 50 \text{ }\mu\text{m}$. These plots show that the 1st term approximation is valid after

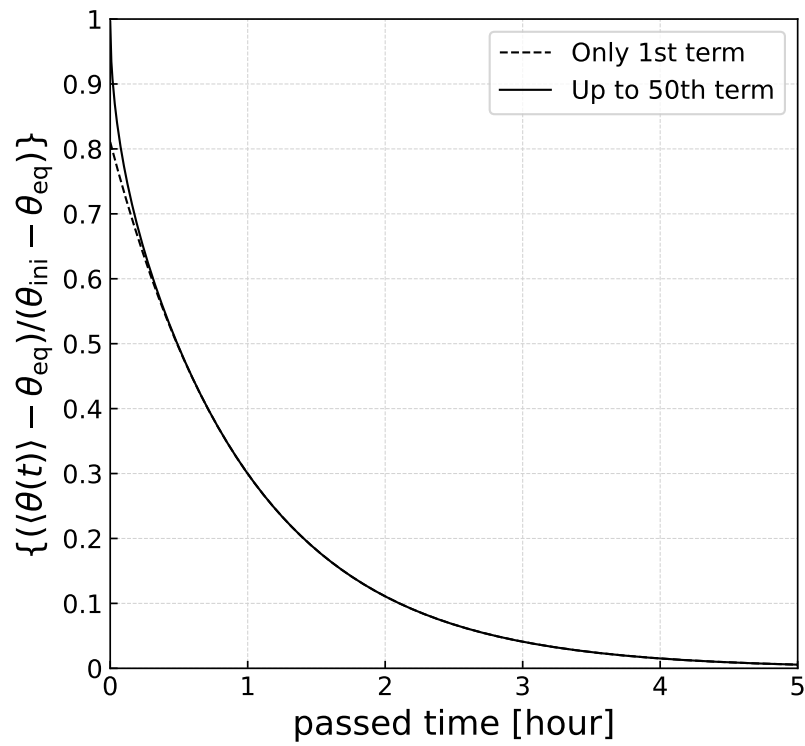


Figure B.1: Compare the 1st order approximation of Eq.(S.B.111) and the summation including higher order terms up to the 50th non-zero term, assuming $D = 7 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and $L = 50 \text{ }\mu\text{m}$.

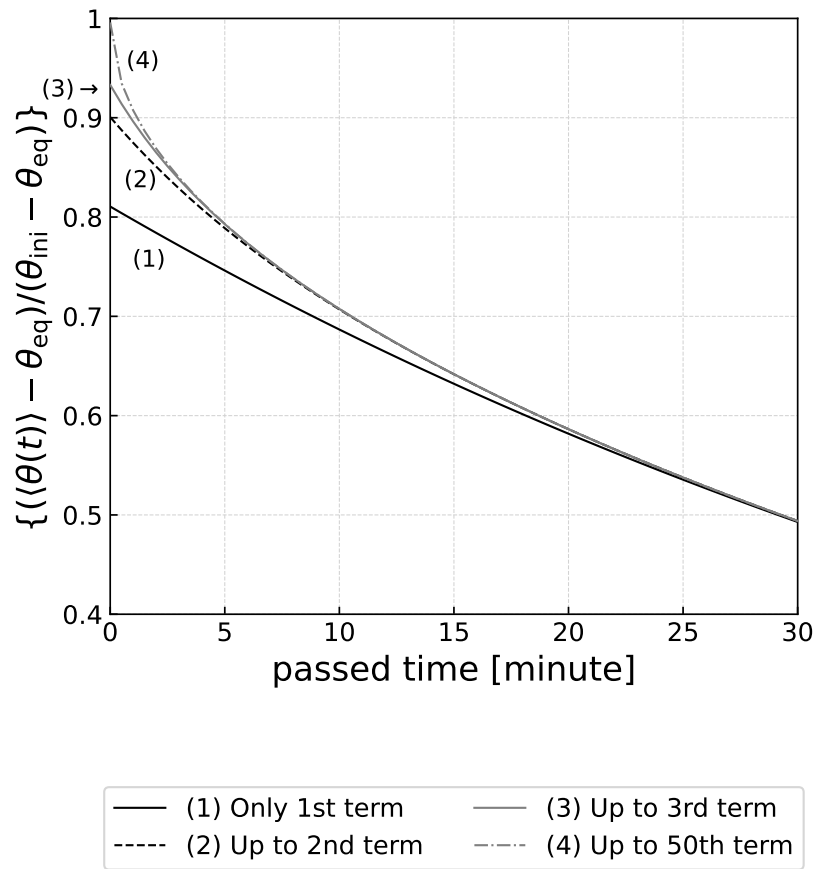


Figure B.2: The comparison of Eq.(S.B.111) with a different number of orders at $0 < t < 30$ [min].

a half of the loading or unloading is achieved, in other words, $t \gtrsim T_{1/2}$. This characteristic time $T_{1/2}$ can be defined as

$$\frac{\langle \theta(t = T_{1/2}) \rangle - \theta_{\text{eq}}}{\theta_{\text{ini}} - \theta_{\text{eq}}} = \frac{1}{2} \quad (\text{S.B.112})$$

Solving this equation for $T_{1/2}$ using the 1st order approximation results in:

$$T_{1/2} = \frac{1}{D} \left(\frac{L}{\pi} \right)^2 \ln \left[\frac{16}{\pi^2} \right] \quad (\text{S.B.113})$$

In case of $D = 7 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$ and $L = 50 \text{ } \mu\text{m}$, we obtain

$$T_{1/2} = 29.1 \text{ minutes} \quad (\text{S.B.114})$$

After this time, the 1st order approximation is valid. Namely,

$$\frac{\langle \theta \rangle - \theta_{\text{eq}}}{\theta_{\text{ini}} - \theta_{\text{eq}}} \sim \frac{8}{\pi^2} e^{-D \left(\frac{\pi}{L} \right)^2 t} \quad (\text{S.B.115})$$

Thus,

$$\ln \left[\frac{\langle \theta \rangle - \theta_{\text{eq}}}{\theta_{\text{ini}} - \theta_{\text{eq}}} \right] \sim -D \left(\frac{\pi}{L} \right)^2 t - \ln \left[\frac{\pi^2}{8} \right] \quad (\text{S.B.116})$$

Therefore,

$$\frac{\partial}{\partial t} \ln \left[\frac{\langle \theta \rangle - \theta_{\text{eq}}}{\theta_{\text{ini}} - \theta_{\text{eq}}} \right] \sim -D \left(\frac{\pi}{L} \right)^2 t \quad (\text{S.B.117})$$

Integrating the original diffusion equation (Eq.(S.B.57)) by x yields:

$$[\text{A}] \int_0^L \frac{\partial \theta(x, t)}{\partial t} dx = - \int_0^L \frac{\partial J(x, t)}{\partial x} dx \quad (\text{S.B.118})$$

$$(\text{S.B.119})$$

where, $J(x, t)$ denotes diffusion flux. Hence,

$$[\text{A}] \frac{\partial}{\partial t} \int_0^L \theta(x, t) dx = [\text{A}] L \frac{\partial}{\partial t} \langle \theta \rangle \quad (\text{S.B.120})$$

$$= J(x = 0, t) - J(x = L, t) \quad (\text{S.B.121})$$

$$= 2J(x = 0, t) \quad (\text{S.B.122})$$

$$= -2J(x = L, t) \quad (\text{S.B.123})$$

Note that we used the relation $J(x=0, t) = -J(x=L, t)$ that results from the symmetry of our system. If we want to define the sorption flux as positive, the total transient flux J_{trans} can be defined as $J_{\text{trans}} \equiv J(x=0, t)$. We can also define the desorption flux as positive by defining as $J_{\text{trans}} \equiv J(x=L, t)$. In this paper, we define the sign of J_{trans} in a way where the desorption flux is expressed as positive. Therefore,

$$[A]L \frac{\partial}{\partial t} \langle \theta \rangle = -2J_{\text{trans}}(t) \quad (\text{S.B.124})$$

Substituting Eq.(S.B.115) into Eq.(S.B.124) yields:

$$J_{\text{trans}}(t) = -\frac{[A]L}{2} \frac{\partial}{\partial t} \left[(\theta_{\text{ini}} - \theta_{\text{eq}}) \frac{4}{\pi^2} e^{-D(\frac{\pi}{L})^2 t} \right] \quad (\text{S.B.125})$$

$$= [A] \frac{4D}{L} (\theta_{\text{ini}} - \theta_{\text{eq}}) e^{-D(\frac{\pi}{L})^2 t} \quad (\text{S.B.126})$$

$$= [A] \frac{4D}{L} \Delta\theta_{\text{trans}} e^{-D(\frac{\pi}{L})^2 t} \quad (\text{S.B.127})$$

where,

$$\Delta\theta_{\text{trans}} \equiv \theta_{\text{ini}} - \theta_{\text{eq}} \quad (\text{S.B.128})$$

The sign of Eq.(Eq.S.B.126) confirms that $J_{\text{trans}}(t)$ is positive (i.e., desorption flux occurs) when $\theta_{\text{ini}} > \theta_{\text{eq}}$ while $J_{\text{trans}}(t)$ is negative (i.e., sorption flux occurs) when $\theta_{\text{ini}} < \theta_{\text{eq}}$.

The subscript trans means that this flux is caused by the transition of the surrounding environment and is time-dependent. The transient flux at $t = T_{1/2} = \frac{1}{D} \left(\frac{L}{\pi}\right)^2 \ln \left[\frac{16}{\pi^2}\right]$ is:

$$J_{\text{trans}T_{1/2}} = [A] \frac{D}{L} \frac{\pi^2}{4} \Delta\theta_{\text{trans}} \quad (\text{S.B.129})$$

By contrast, if the concentration gradient $\Delta\theta_{\text{pump}}$ is kept across the flat sheet, there should be a time-independent steady continuous flux from one side to the other, J_{pump} :

$$J_{\text{pump}} = [A] \frac{D}{L} \Delta\theta_{\text{pump}} \quad (\text{S.B.130})$$

where,

$$\Delta\theta_{\text{pump}} \equiv \theta(x=0) - \theta(x=L) \quad (\text{S.B.131})$$

Therefore, there is the following relation between J_{trans} and J_{pump} :

$$J_{\text{pump}} \sim \left(\frac{4}{\pi^2}\right) \left(\frac{\Delta\theta_{\text{pump}}}{\Delta\theta_{\text{trans}}}\right) J_{\text{trans}} T_{1/2} \quad (\text{S.B.132})$$

B.3 Analytic solution for a dynamic steady-state

We can derive an analytic solution for Eq.(S.B.32) in a dynamic steady-state in case we can regard D_C and D_D as a constant. In a steady-state, Eq.(S.B.32) can be transformed into the following 2nd-order ODE:

$$0 = -\frac{d}{dx} \left(-D_{\text{eff}}(\theta) \frac{d\theta}{dx} \right) \quad (\text{S.B.133})$$

Integrating this 2nd-order ODE by x once yields:

$$c_1 = D_{\text{eff}}(\theta) \left(\frac{d\theta}{dx} \right) \quad (\text{S.B.134})$$

Or,

$$c_1 = \frac{D_C D_D}{D_C - 2D_D} \left(-1 + \frac{2(D_C - D_D)}{2\theta(D_C - D_D) - (D_C - 4D_D)} \right) \left(\frac{d\theta}{dx} \right) \quad (\text{S.B.135})$$

where, c_1 is the constant of integration. Note that c_1 has a physical meaning as the total carbon flux J_{carbon} normalized by $-[A]$, namely:

$$J_{\text{carbon}} = -c_1[A] \quad (\text{S.B.136})$$

Now, Eq.(S.B.135) can be rearranged into:

$$d\theta \left(-1 + \frac{2(D_C - D_D)}{2\theta(D_C - D_D) - (D_C - 4D_D)} \right) = dx \left(\frac{c_1(D_C - 2D_D)}{D_C D_D} \right) \quad (\text{S.B.137})$$

Integrating this 1st-order ODE yields:

$$-\theta + \frac{D_C - D_D}{D_C - 2D_D} \times \ln [2\theta(D_C - D_D) - (D_C - 4D_D)] = \frac{c_1 x (D_C - 2D_D)}{D_C D_D} + c_2 \quad (\text{S.B.138})$$

where, c_2 is the constant of integration. These constants c_1 and c_2 can be expressed using the boundary conditions. Now, we consider the following boundary conditions determined by $K_{\text{eq}(\text{eff})}$ (or relative humidity, RH) and P_{CO_2} :

$$\theta(x=0) = \theta_{\text{eq}}(P_{\text{CO}_2}(x=0); K_{\text{eq}(\text{eff})}(\text{RH}(x=0))) \quad (\text{S.B.139})$$

$$\equiv \theta_0 \quad (\text{S.B.140})$$

$$\theta(x=L) = \theta_{\text{eq}}(P_{\text{CO}_2}(x=L); K_{\text{eq}(\text{eff})}(\text{RH}(x=L))) \quad (\text{S.B.141})$$

$$\equiv \theta_L \quad (\text{S.B.142})$$

Then, C_1 and C_2 can be derived as:

$$c_1 = \frac{D_C D_D}{L(D_C - 2D_D)} \{ -(\theta_L - \theta_0) + \frac{D_C - D_D}{D_C - 2D_D} \times \ln \left[\frac{2\theta_L(D_C - 2D_D) - (D_C - 4D_D)}{2\theta_0(D_C - 2D_D) - (D_C - 4D_D)} \right] \} \quad (\text{S.B.143})$$

$$c_2 = -\theta_0 + \frac{D_C - D_D}{D_C - 2D_D} \times \ln [2\theta_0(D_C - 2D_D) - (D_C - 4D_D)] \quad (\text{S.B.144})$$

Substituting these expressions of A and B into Eq.(S.B.138) yields:

$$\begin{aligned} & -(\theta - \theta_0) + \frac{D_C - D_D}{D_C - 2D_D} \times \ln \left[\frac{2\theta(D_C - 2D_D) - (D_C - 4D_D)}{2\theta_0(D_C - 2D_D) - (D_C - 4D_D)} \right] \\ & = \frac{x}{L} \left\{ -(\theta_L - \theta_0) + \frac{D_C - D_D}{D_C - 2D_D} \times \ln \left[\frac{2\theta_L(D_C - 2D_D) - (D_C - 4D_D)}{2\theta_0(D_C - 2D_D) - (D_C - 4D_D)} \right] \right\} \end{aligned} \quad (\text{S.B.145})$$

This is the analytic solution for θ in a dynamic steady-state. The continuous CO_2 pumping flux J_{pump} can be expressed as:

$$\begin{aligned} J_{\text{pump}}(D_C, D_D) & = -c_1[A] \quad (\text{S.B.146}) \\ & = -\frac{D_C D_D}{L(D_C - 2D_D)} [A] \{ -(\theta_L - \theta_0) + \frac{D_C - D_D}{D_C - 2D_D} \times \ln \left[\frac{2\theta_L(D_C - 2D_D) - (D_C - 4D_D)}{2\theta_0(D_C - 2D_D) - (D_C - 4D_D)} \right] \} \end{aligned} \quad (\text{S.B.147})$$

This is the analytic expression for J_{pump} .

Note that, in case of $D_C \sim D_D (\equiv D)$, then, Eq.(S.B.145) results in:

$$\frac{\theta - \theta_0}{\theta_L - \theta_0} = \frac{x}{L} \quad (\text{S.B.148})$$

This is just a straight line, which is the solution for the linear diffusion equation in a steady state. In this case, the CO_2 pumping flux J_{pump} can be approximated to:

$$J_{\text{pump}}(D_C \sim D_D (\equiv D)) = -D \left(\frac{\theta_L - \theta_0}{L} \right) [A] \quad (\text{S.B.149})$$

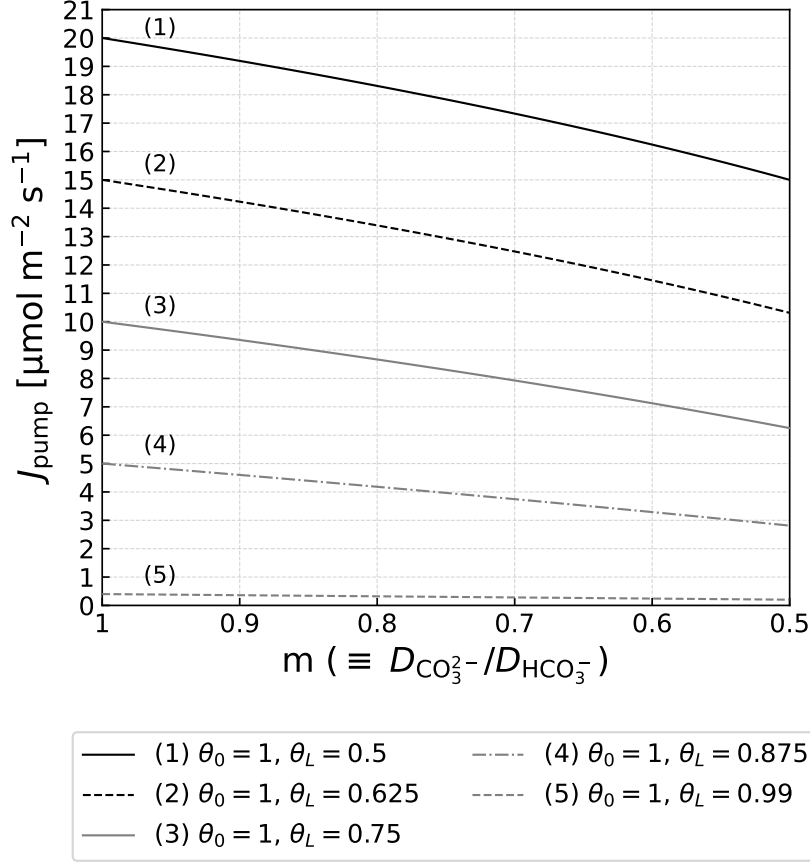


Figure B.3: J_{pump} (or the CO_2 pumping flux) assuming $D_{\text{HCO}_3^-} = 1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $L = 50 \text{ }\mu\text{m}$ and $[\text{A}] = 2 \text{ mmol cm}^{-3}$.

Fig.(B.3) shows the calculated J_{pump} against $m \equiv D_{\text{CO}_3^{2-}}/D_{\text{HCO}_3^-}$ based on Eq.(S.B.147), assuming $D_{\text{HCO}_3^-} = 1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$, $L = 50 \text{ }\mu\text{m}$ and $[\text{A}] = 2 \text{ mmol cm}^{-3}$. This plot describes how the amplitude of a continuous CO_2 pumping flux is hampered when the diffusivity of CO_3^{2-} is smaller than HCO_3^- . For example, this plot suggests that if $D_{\text{HCO}_3^-}$ is $\sim 1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ and $(\theta_0, \theta_L) = (1, 0.75)$, an expected amplitude of J_{pump} ranges from 6.3 to 10.0 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ for a membrane with thickness of 50 μm as long as $0.5 < m < 1$.

In case that the changes in $D_{\text{HCO}_3^-}$ and $D_{\text{CO}_3^{2-}}$ depending on the water uptake in the AEM are not negligible, one needs to solve the first-order ODE (Eq.(S.B.137)) numerically.

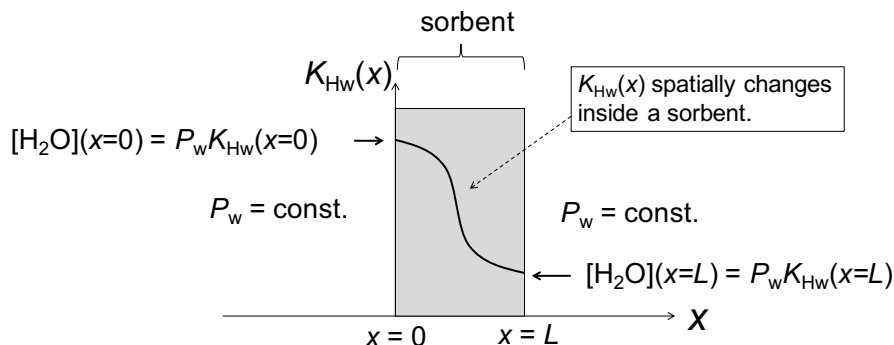


Figure B.4: A graphical explanation of a one-dimensional system where an equilibrium constant spatially changes inside a sorbent.

B.4 Activity, concentration and a perpetual motion machine

We consider a simple system with a polymer matrix that binds water and the bound water is mobile and can diffuse through polymer matrix. The polymer forms a membrane which either side is in contact with water vapor. The binding energy between water and the polymer matrix or a sorbent can be described by an equilibrium coefficient. We assume that material properties of the polymer matrix change with position. Therefore, the equilibrium coefficient is not really constant but depends on locations. We imagine a simple one-dimensional system along x -axis in which the sorbent is located at the location $0 < x < L$ (see Fig.(B.4)). The sorbent sorbs and desorbs water from and to the surrounding environment through its surface at $x = 0$ and $x = L$ according to Henry's law. The concentration of water in a sorbent, $[\text{H}_2\text{O}]$, can be expressed using a Henry's constant K_{Hw} and partial pressure of vapor in the surrounding environment P_w as:

$$[\text{H}_2\text{O}] = K_{\text{Hw}} P_w \quad (\text{S.B.150})$$

P_w is constant and equal at the two sides of the flat sheet. Henry's constant K_{Hw} depends on a standard chemical potential of water inside the polymer. If the material property changes across the membrane, Henry's constant on the two sides of the membrane are different. As a consequence, there must be a gradient in water concentration inside a membrane. This gradient in turn supports a flux, which violates the second law.

C

Experimental section

C.1 Titration theory

We consider the procedure to measure the amount of counter ion CO_3^{2-} attached to the commercial AEM. First, we soak AEM into high-concentration (e.g. 1[M]) NaCl solution. Due to the mass action law, most of the counter ion should be replaced with Cl^- . Therefore,

$$[\text{Cl}^-]_{\text{to AEM}} = [\text{IEC}]_{\text{AEM}} \quad (\text{S.C.1})$$

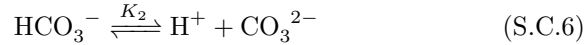
$$\begin{aligned} &= [\text{HCO}_3^-]_{\text{released from AEM}} \\ &\quad + 2[\text{CO}_3^{2-}]_{\text{released from AEM}} \end{aligned} \quad (\text{S.C.2})$$

where, the subscript to AEM means the amount attached into the AEM, the subscript initial means the initial concentration just before the titration (but after soaking the AEM in the NaCl solution and after finishing the counter ion replacement) and the subscript released from AEM means the amount released from the AEM sample into the NaCl solution. If we define the initial concentration of the DICl (Dissolved Inorganic Carbon as Ions) as $[\text{DICl}]_{\text{initial}}$, the conservation law of carbon results in:

$$[\text{DICl}]_{\text{initial}} = [\text{DICl}]_{\text{released from AEM}} \quad (\text{S.C.3})$$

$$\begin{aligned} &= [\text{HCO}_3^-]_{\text{released from AEM}} \\ &\quad + [\text{CO}_3^{2-}]_{\text{released from AEM}} \end{aligned} \quad (\text{S.C.4})$$

Note that we neglect the CO_2 dissolution from the ambient air during the titration experiment because the titration procedure can be typically completed within a couple of hours. We consider the following chemical equilibria:



where,

$$K_W \equiv [\text{H}_{(\text{aq})}^+][\text{OH}_{(\text{aq})}^-] \quad (\text{S.C.8})$$

$$K_1^* \equiv \frac{[\text{H}_{(\text{aq})}^+][\text{HCO}_{3(\text{aq})}^-]}{[\text{H}_2\text{CO}_{3(\text{aq})}]^*} \quad (\text{S.C.9})$$

$$K_2 \equiv \frac{[\text{H}_{(\text{aq})}^+][\text{CO}_{3(\text{aq})}^{2-}]}{[\text{HCO}_{3(\text{aq})}^-]} \quad (\text{S.C.10})$$

$$[\text{H}_2\text{CO}_{3(\text{aq})}]^* \equiv [\text{H}_2\text{CO}_{3(\text{aq})}] + [\text{CO}_{2(\text{aq})}] \quad (\text{S.C.11})$$

$$[\text{HCO}_3^-(\text{aq})] = [\text{H}_2\text{CO}_3(\text{aq})]^* \frac{K_1^*}{[\text{H}^+]} \quad (\text{S.C.12})$$

$$[\text{CO}_3^{2-}(\text{aq})] = [\text{H}_2\text{CO}_3(\text{aq})]^* \frac{K_1^* K_2^*}{[\text{H}^+]^2} \quad (\text{S.C.13})$$

If we define the initial concentration of DICl (Dissolved Inorganic Carbon as Ions) as $[\text{DICl}]_{\text{initial}}$, then the conservation law of carbon results in:

$$[\text{DICl}]_{\text{initial}} = [\text{H}_2\text{CO}_3(\text{aq})]^* + [\text{HCO}_3^-(\text{aq})] + [\text{CO}_3^{2-}(\text{aq})] \quad (\text{S.C.14})$$

$$= [\text{H}_2\text{CO}_3(\text{aq})]^* \times \left(1 + \frac{K_1^*}{[\text{H}^+]} + \frac{K_1^* K_2^*}{[\text{H}^+]^2} \right) \quad (\text{S.C.15})$$

Therefore,

$$[\text{H}_2\text{CO}_3(\text{aq})]^* = \frac{[\text{DICl}]_{\text{initial}}}{1 + \frac{K_1^*}{[\text{H}^+]} + \frac{K_1^* K_2^*}{[\text{H}^+]^2}} \quad (\text{S.C.16})$$

$$[\text{HCO}_3^-(\text{aq})] = \frac{K_1^*}{[\text{H}^+]} \times \frac{[\text{DICl}]_{\text{initial}}}{1 + \frac{K_1^*}{[\text{H}^+]} + \frac{K_1^* K_2^*}{[\text{H}^+]^2}} \quad (\text{S.C.17})$$

$$[\text{CO}_3^{2-}(\text{aq})] = \frac{K_1^* K_2^*}{[\text{H}^+]^2} \times \frac{[\text{DICl}]_{\text{initial}}}{1 + \frac{K_1^*}{[\text{H}^+]} + \frac{K_1^* K_2^*}{[\text{H}^+]^2}} \quad (\text{S.C.18})$$

Then, the condition of charge neutrality is:

$$[\text{H}^+] + \cancel{[\text{Na}^+]_{\text{original}}} \quad (\text{S.C.19})$$

$$= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] \quad (\text{S.C.20})$$

$$+ \cancel{[\text{Cl}^-]_{\text{original}}} - [\text{Cl}^-]_{\text{to AEM}} + [\text{Cl}^-]_{\text{added}} \quad (\text{S.C.21})$$

where, the subscript original means the concentration before soaking the AEM sample in the NaCl solution. For example, if we use 1 mol L⁻¹ of NaCl solution, then, $[\text{Na}^+]_{\text{original}} = [\text{Cl}^-]_{\text{original}} = 1 \text{ mol L}^{-1}$.

Now $[\text{Cl}^-]_{\text{toAEM}} = [\text{HCO}_3^-]_{\text{released from AEM}} + 2[\text{CO}_3^{2-}]_{\text{released from AEM}}$, so,

$$\begin{aligned}
& [\text{Cl}^-]_{\text{added}} \\
= & [\text{H}^+] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] \\
& + [\text{HCO}_3^-]_{\text{released from AEM}} + 2[\text{CO}_3^{2-}]_{\text{released from AEM}} \tag{S.C.22}
\end{aligned}$$

$$\begin{aligned}
= & [\text{H}^+] \\
& - \left(\frac{K_1}{[\text{H}^+]} + 2 \frac{K_1^* K_2}{[\text{H}^+]^2} \right) \times \frac{[\text{DICI}]_{\text{initial}}}{1 + \frac{K_1^*}{[\text{H}^+]} + \frac{K_1^* K_2}{[\text{H}^+]^2}} \\
& - \frac{K_W}{[\text{H}^+]} \\
& + [\text{HCO}_3^-]_{\text{released from AEM}} + 2[\text{CO}_3^{2-}]_{\text{released from AEM}} \tag{S.C.23}
\end{aligned}$$

$$\begin{aligned}
= & [\text{H}^+] \\
& - \left(\frac{K_1}{[\text{H}^+]} + 2 \frac{K_1^* K_2}{[\text{H}^+]^2} \right) \times \frac{[\text{HCO}_3^-]_{\text{released from AEM}} + [\text{CO}_3^{2-}]_{\text{released from AEM}}}{1 + \frac{K_1^*}{[\text{H}^+]} + \frac{K_1^* K_2}{[\text{H}^+]^2}} \\
& - \frac{K_W}{[\text{H}^+]} \\
& + [\text{HCO}_3^-]_{\text{released from AEM}} + 2[\text{CO}_3^{2-}]_{\text{released from AEM}} \tag{S.C.24}
\end{aligned}$$

Eq.(S.C.24) shows that $[\text{Cl}^-]_{\text{added}}$ can be expressed as a function of pH and vice versa. Fig.(C.1) shows the theoretical titration curve based on Eq.(S.C.24). This plot is calculated assuming that 100 μmol of HCO_3^- and 50 μmol of CO_3^{2-} (i.e., 150 μmol of DICI and 200 μmol of ion exchange capacity) are released from the AEM sample into 200 mL of NaCl solution. The concentration of the HCl for the titration is assumed to be 0.1 mol L^{-1} . As is well-known, we can see the buffer zone around $\text{pH}=6 \sim 7$ in this theoretical titration curve. If we define the pH value at the middle of this buffer zone as $\text{pH}_{\text{buffer}}$, it can be expressed as:

$$\left. \frac{d^2[\text{Cl}^-]_{\text{added}}}{d\text{pH}^2} \right|_{\text{pH}=\text{pH}_{\text{buffer}}} = 0 \tag{S.C.25}$$

In this buffer zone, $[\text{CO}_3^{2-}]$, $[\text{OH}^-]$ and $[\text{H}^+]$ are negligible since the solution is almost neutral. Therefore,

$$[\text{HCO}_3^-]_{\text{(aq)}} \sim \frac{K_1^*}{[\text{H}^+]} \times \frac{[\text{DICI}]_{\text{initial}}}{1 + \frac{K_1^*}{[\text{H}^+]}} \tag{S.C.26}$$

$$[\text{CO}_3^{2-}]_{\text{(aq)}} \sim 0 \tag{S.C.27}$$

Therefore,

$$\frac{d^2[\text{Cl}^-]_{\text{added}}}{d\text{pH}^2} \sim -\frac{d^2[\text{HCO}_3^-(\text{aq})]}{d\text{pH}^2} \quad (\text{S.C.28})$$

Now, by definition, we have the following relations:

$$\text{pH} \equiv -\log_{10}[\text{H}^+] \quad (\text{S.C.29})$$

and

$$\frac{d\text{pH}}{d[\text{H}^+]} = -\frac{1}{[\text{H}^+]} \frac{1}{\ln 10} \quad (\text{S.C.30})$$

Substituting these into $\frac{d^2[\text{HCO}_3^-(\text{aq})]}{d\text{pH}^2}$ yields:

$$\frac{d^2[\text{Cl}^-]_{\text{added}}}{d\text{pH}^2} \sim -(\ln 10)^2 [\text{DICI}]_{\text{initial}} \frac{K_1^*([\text{H}^+] - K_1^*)}{([\text{H}^+] + K_1^{*2})^3} \quad (\text{S.C.31})$$

Namely,

$$\text{pH}_{\text{buffer}} = -\log_{10} K_1^* \quad (\text{S.C.32})$$

$$= 6.35 \text{ (at } T = 25^\circ\text{C)} \quad (\text{S.C.33})$$

Fig.(C.1) also indicates that there are sharp pH decreases before and after this buffer area. The first sharp decrease shows that all the CO_3^{2-} in the solution has been consumed and the second sharp decrease shows that all the HCO_3^- in the solution has been consumed by chemical reactions. So, if we define the amount of Cl^- ion that is added by the titration up to the first and the second sharp pH decrease zones as $x[\text{mol}]$ and $2x + y[\text{mol}]$, then,

$$x = \text{CO}_3^{2-} \text{ released from AEM [mol]} \quad (\text{S.C.34})$$

$$2x + y = 2\text{CO}_3^{2-} \text{ released from AEM [mol]} \quad (\text{S.C.35})$$

$$+\text{HCO}_3^- \text{ released from AEM [mol]} \quad (\text{S.C.36})$$

Therefore,

$$\text{CO}_3^{2-} \text{ released from AEM} = x \text{ [mol]} \quad (\text{S.C.37})$$

$$\text{HCO}_3^- \text{ released from AEM} = y \text{ [mol]} \quad (\text{S.C.38})$$

$$\text{DICI}_{\text{released from AEM}} = x + y \text{ [mol]} \quad (\text{S.C.39})$$

$$\text{IEC}_{\text{released from AEM}} = 2x + y \text{ [mol]} \quad (\text{S.C.40})$$

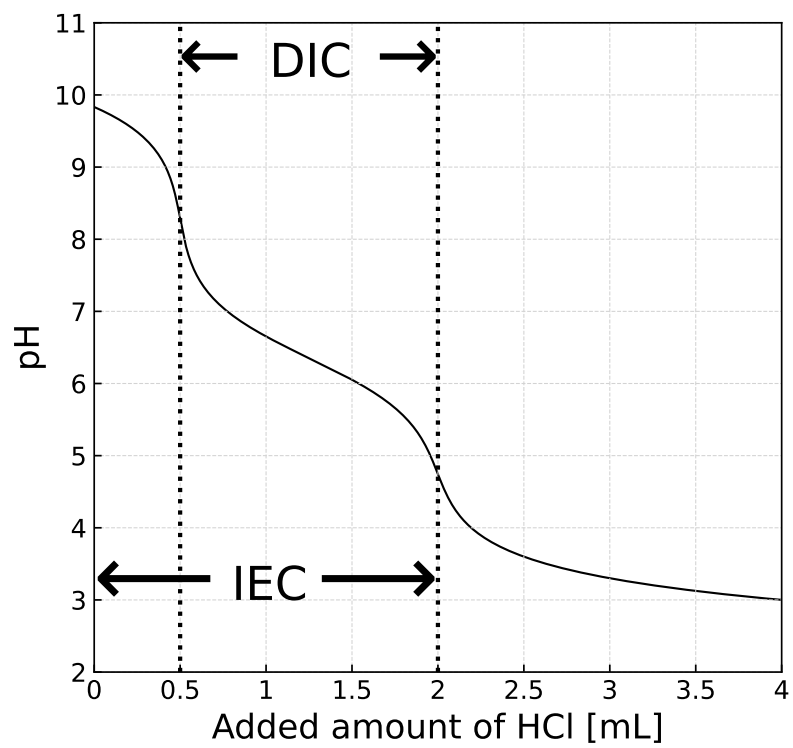


Figure C.1: Theoretical titration curve (Eq.(S.C.24)) assuming that $100 \mu\text{mol}$ of HCO_3^- and $50 \mu\text{mol}$ of CO_3^{2-} are released from the AEM sample into 200 mL of NaCl solution. The concentration of the HCl used for the titration is assumed to be 0.1 mol L^{-1} . The two vertical lines show the points where the CO_3^{2-} or the HCO_3^- in the solution is completely consumed by the chemical reaction with the HCl , respectively.

C.2 Titration experiment

We soak a preconditioned sample into 500 mL of a 1 mol L⁻¹ NaCl aqueous solution. The counter ions contained in an AEM are transferred into the solution. An equivalent amount of chloride ions moves from the solution to the AEM, in order to maintain charge balance. We can measure this lost amount of chloride by titration using 0.1 mol L⁻¹ hydrochloric acid. Furthermore, charge conservation enable us to distinguish between [HCO₃⁻] and [CO₃²⁻] in this titration experiment data.

Fig.(C.2) shows the measured titration data for a dry tiny sample (weight: 0.0694 dry-g) and a wet tiny sample (weight: 0.089 dry-g), using the Industrial pH probe (model: ENV-50-pH) made by Atlas Scientific. Both of the experimental data are consistent with the theoretical model of an ideal solution except for some vertical bulk shift. There are some possible reasons of the vertical shift, e.g., the non-perfect calibration of a pH probe or an influence from an ionic strength. However, since we are only interested in where the sharp decrease of pH occurs, very accurate pH values are not necessary. The second titration result of the wet sample indicates there is no appreciable amount of the DIC left behind, which confirms that all the DIC derived from these AEM samples has been titrated in the first titration. Table.(C.1) summarizes the measured amount of DIC, IEC and θ of the dry and wet sample.

The observed change of θ between a wet and a dry sample mean that the preconditioned Fumasep® FAA-3-50 works as a moisture-controlled CO₂ sorbent. The measured IEC per sample weight is 1.73±0.14 mmol/dryAEM-g for the dry sample and 1.35±0.11 mmol/dryAEM-g for the wet sample, both of which are comparable to the values in the manufacturer's technical datasheet, 1.6-2.0 mmol/dryAEM-g.

This titration curve has a buffer zone at pH = 6.35 (at $T = 25$ °C). It also indicates that there are sharp pH decreases before and after the buffer area. The first sharp decrease shows that all the CO₃²⁻ in the solution has been consumed and the second sharp decrease shows that all the HCO₃⁻ in the solution has been consumed by the titrant. So, if we define the amount of chloride ion that is added by the titration up to the first and the second sharp pH decrease zones as x and y , the DIC and the IEC can be derived as

$$\text{DIC}_{\text{AEM}} = y - x \quad (\text{S.C.41})$$

$$\text{IEC}_{\text{AEM}} = y \quad (\text{S.C.42})$$

Also, the amount of the counterion initially attached to the AEM sample can be derived as

$$\text{CO}_3^{2-}_{\text{AEM}} = x \quad (\text{S.C.43})$$

$$\text{HCO}_3^{-}_{\text{AEM}} = y - 2x \quad (\text{S.C.44})$$

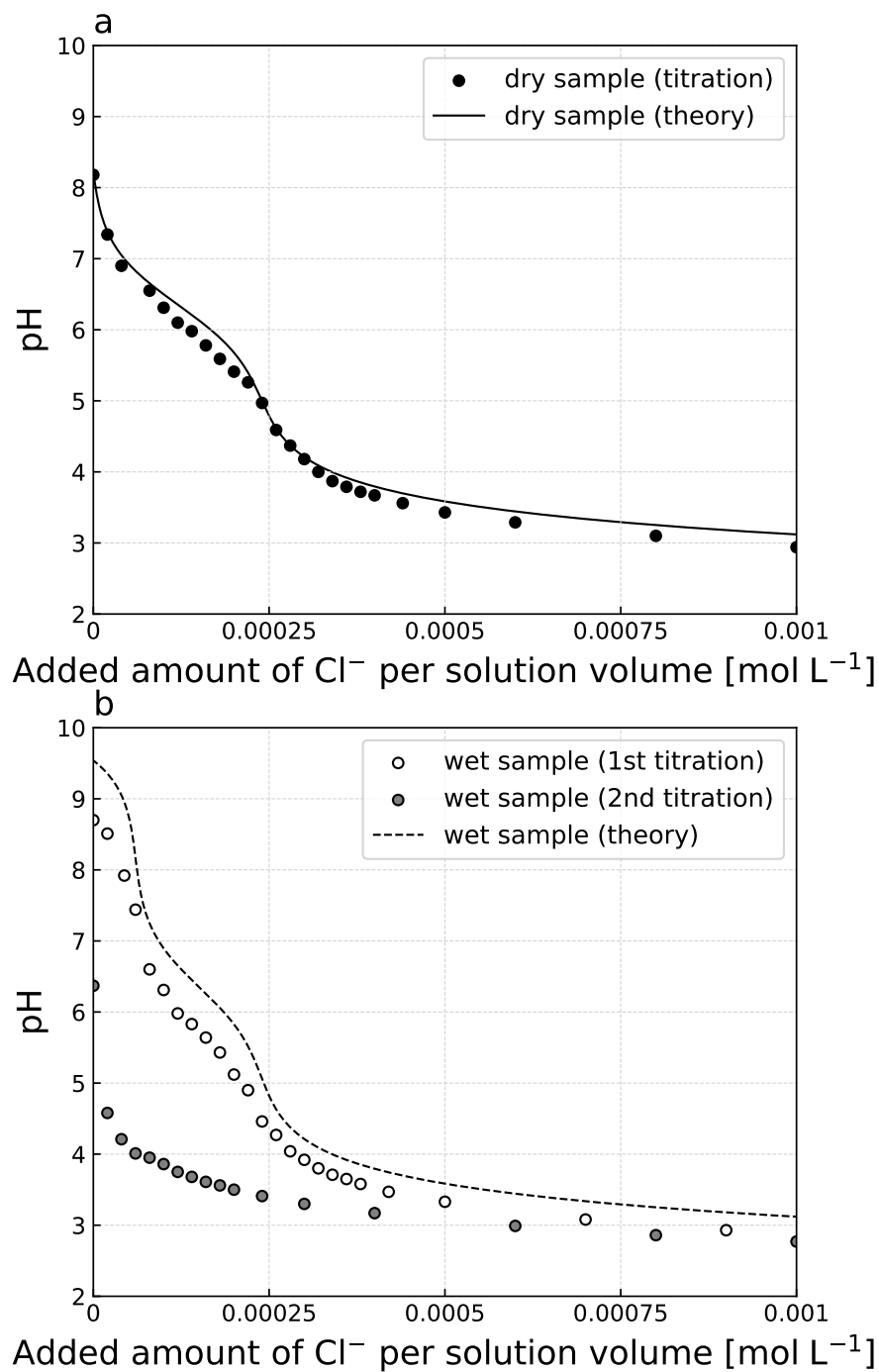


Figure C.2: Titration results; (a) for a dry membrane and (b) for a wet membrane.

In this section, a dry sample means that the sample is equilibrated with the ambient air in the lab overnight while a wet sample indicates that the sample is directly soaked into a DI water after being dried.

The comparison to the theoretical lines suggests that wet sample has 120 ± 10 μmol of IEC and 90 ± 10 μmol of DIC (namely, $\theta \sim 0.75 \pm 0.08$) while the dry sample has 120 ± 10 μmol of IEC and 120 ± 10 μmol of DIC (namely, $\theta \sim 1 \pm 0.12$).

Table C.1: Summary of the measured amount of DIC, IEC and θ in the original samples by titration.

| sample status | DIC [μmol] | IEC [μmol] | θ | sample weight [dry-g] |
|---------------|-------------------------|-------------------------|-----------------|-----------------------|
| dry | 120 ± 10 | 120 ± 10 | 1 ± 0.12 | 0.0694 |
| wet | 90 ± 10 | 120 ± 10 | 0.75 ± 0.08 | 0.089 |

C.3 Main experimental setup and instruments

Some photos of the main experiment apparatus are shown in Fig.(C.3), Fig.(C.4) and Fig.(C.5). In the following, we explain the stages of the flow lines from the gas cylinders to the end one by one.

From gas cylinders to mass flow controllers. We prepare two gas cylinders: a pure N_2 cylinder and a mixed gas cylinder of 80% N_2 and 20% CO_2 . The gas flow from the former cylinder is split into four flow lines, two of which goes through bubblers to generate wet N_2 gas lines while the other two lines remain dry. The gas flow from the mixed gas cylinder is split into two lines. So, we have two sets of the following three lines: (1) dry N_2 gas, (2) wet N_2 gas and (3) dry N_2 (80%)- CO_2 (20%) mixture gas. These three gases flow into mass flow controllers (MFC) so that we can control concentrations of H_2O and CO_2 in the two feed gas lines as we desire. The model of the MFCs used for dry and wet N_2 gases are MC-100SCCM-D and the ones for dry N_2 (80%)- CO_2 (20%) mixture gas are the MC-10SCCM-D-A019, both of which are made by Alicat Scientific. MC-100SCCM has a calibrated range of 0-100 SCCM (Standard Cubic Centimeters / Minute), and the MC-10SCCM-D-A019 has a calibrated range of 0-10 SCCM. Each has 5 digits of resolution. Note that the STP (standard temperature and pressure) are $25^\circ C$ and 1 atm. The CO_2 concentration in the feed gas is set to be a constant value at the ambient level (i.e. 400 ppm) throughout the experiments.

From mass flow controllers to Infrared Gas Analyzers. After passing through the MFCs, the six flow lines go into a custom acrylic box covered with thermal insulation, in which the temperature is roughly controlled to be slightly above $35^\circ C$ to avoid water condensation inside the flow lines (see Fig.(C.3)). This acrylic box has three separate compartments: one for bubblers, one for Infrared Gas Analyzers and one for a membrane sample holder. A heater (200W), a fan and a temperature probe for temperature control is contained in each compartment so that we can regulate the temperature in each compartment to $35^\circ C$. For more accurate temperature control, the bubblers and the membrane holder are immersed in water baths. The temperature of these water baths are controlled to be $35.0 \pm 0.2^\circ C$ using Cole-Parmer StableTemp Ceramic Stirring Hot Plates (see Fig.(C.4)). After heat exchange in the water bath, only the two N_2 lines go thorough the bubblers in the water bath, which generate water-saturated N_2 feed gas at $35^\circ C$. The three lines are merged to generate the feed gas for one part of the sample holder (top cell); the other three lines are merged for the feed gas for the other side of the membrane holder (bottom cell). These two feed lines go into Infrared Gas Analyzers (IRGA) in the next compartment. H_2O and CO_2 concentrations are measured simultaneously by IRGAs. The IRGAs are LI-840 and LI-840A made by LI-COR.

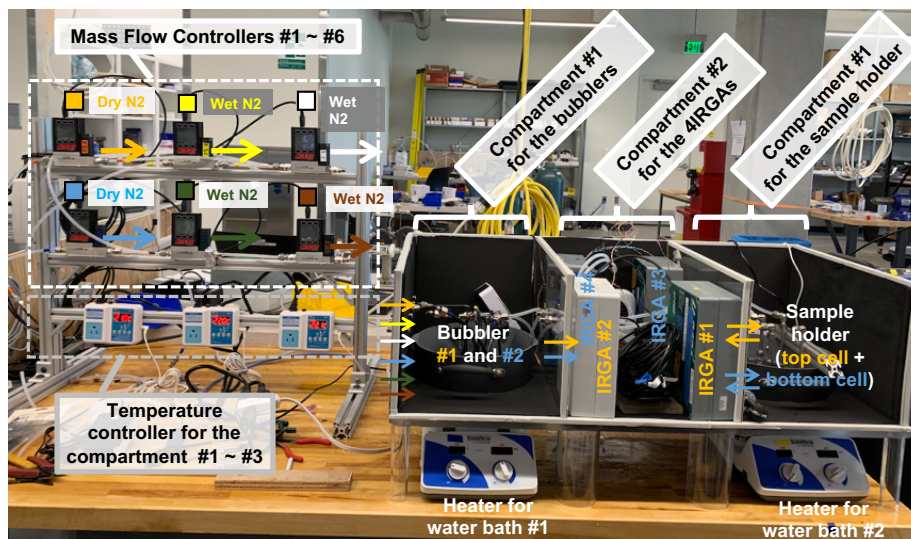


Figure C.3: A photo of the whole experiment setup without the lids of the acrylic box.

From Infrared Gas Analyzers to the membrane sample holder. The two lines go to the next compartment and are fed to the top cell and the bottom cell of the membrane holder in the water bath, respectively. The custom membrane holder consists of the two cells: the top half cell and the bottom half cell. They are cylindrical cells with inner diameter of 7 cm. The open volume in each half cell is about 120 cm^3 . The geometry of these cells is the same except that the bottom cell have an inlet and outlet port on the wall while the top cell does not. The top side and the bottom side of the membrane holder are covered with acrylic plates of half-inch thickness during experiments. The top acrylic lid has an inlet and outlet port for the top cell. The sample membrane is sandwiched between two custom Viton gasket with inner diameter of 7 cm and outer diameter of 10 cm. These gaskets are impermeable for both H_2O and CO_2 . The thickness of each gasket is 3 mm. The nominal membrane area is the same as the area inside the inner circle of the gasket, i.e., 38.5 cm^2 . Both the top cell and the bottom cell have a 1mm-depth recess to accommodate the gasket in the center. The outlet lines from the top cell and the bottom cell go back to the next compartment and pass through IRGAs to measure the H_2O and CO_2 concentrations in the exit streams. In total, we use four IRGAs and we refer to these as IRGA1, IRGA2, IRGA3 and IRGA4. Finally, the gases are released into the environment outside the acrylic box. Since the flow resistance is small, the total pressure throughout each line is approximately the ambient pressure in the lab.

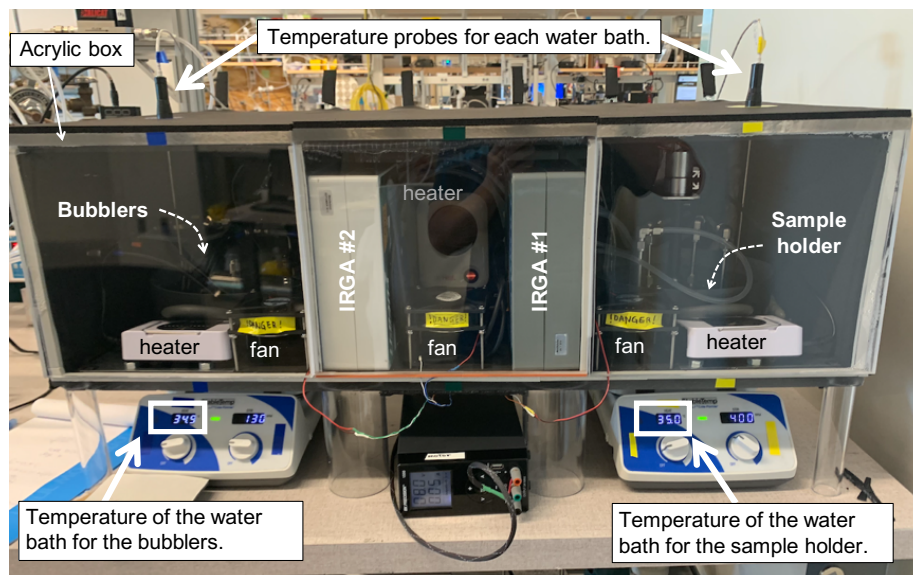


Figure C.4: A photo of the acrylic box during an experiment. The temperatures of the water baths are controlled to be $35.0 \pm 0.2^\circ\text{C}$.

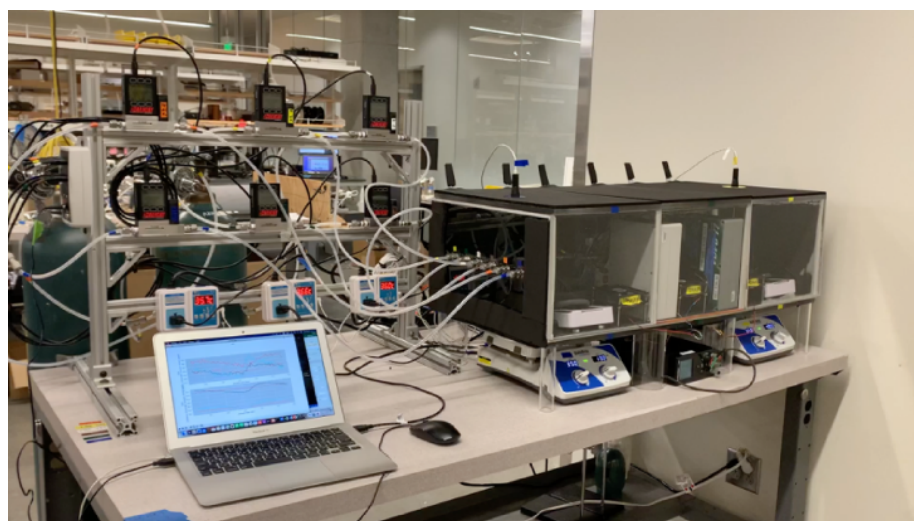


Figure C.5: A photo of the whole experiment apparatus during an experiment.

C.4 Control experiment: correction for the dilution due to addition of vapor

If we add water vapor through bubblers to the feed gas with a constant flow rate, the CO_2 in the flow line after the bubblers is slightly diluted. In these experiments, we prefer to express the CO_2 concentration relative to dry gas rather than total amount of gas. Consequently, we apply the following correction to the raw IRGA readings:

$$\text{CO}_{2\text{cor}}[\text{ppm}] = \frac{\text{CO}_{2\text{raw}}[\text{ppm}]}{1 - \frac{\text{H}_2\text{O}_{\text{raw}}[\text{ppt}]}{1000}} \quad (\text{S.C.45})$$

As a control experiment, we measured H_2O and CO_2 concentrations in IRGA1, IRGA2, IRGA3 and IRGA4 using the same custom membrane holder and bubblers without a sample membrane held in the membrane holder. During the control experiment, we maintain at the ambient temperature in the lab ($T = 22.2 \pm 0.2^\circ\text{C}$). The inlet humidity for one flow line (for IRGA1 and IRGA2) is increased from dry to wet while the inlet humidity in the other flow line (for IRGA3 and IRGA4) is kept the same, as is shown in Fig.(C.6). This plot confirms that the humidity in the two outlet flows (IRGA2 and IRGA4) are equivalent to the average of the two inlet flows (IRGA1 and IRGA3) because there is no membrane to prevent mixing in this control experiment. Fig.(C.7), Fig.(C.8), Fig.(C.9) and Fig.(C.10) compare the CO_2 concentration before and after the correction has been applied. The raw CO_2 data from the IRGAs before the correction clearly show CO_2 jumps at the points where the inlet humidity is changed. After the correction, discontinuous CO_2 jumps disappear. The influence of the bubblers on the CO_2 concentrations are properly compensated by Eq.(S.C.45).

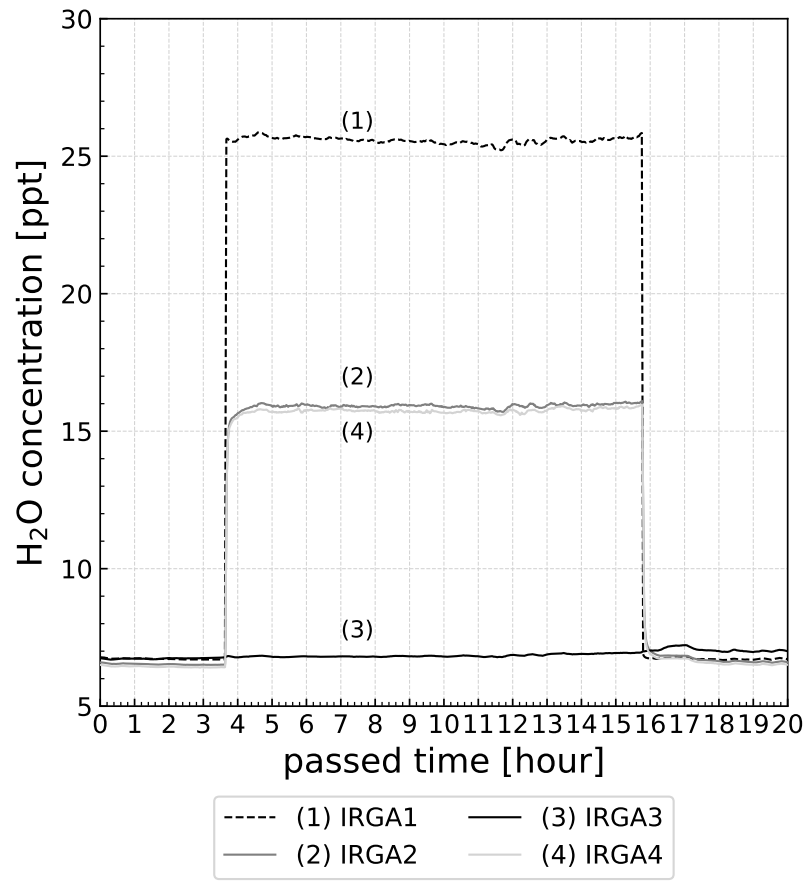


Figure C.6: The inlet humidity profiles (IRGA1 and IRGA3) and the observed outlet humidity profiles (IRGA2 and IRGA4) in the control experiment at $T = 22.2 \pm 0.2^\circ\text{C}$.

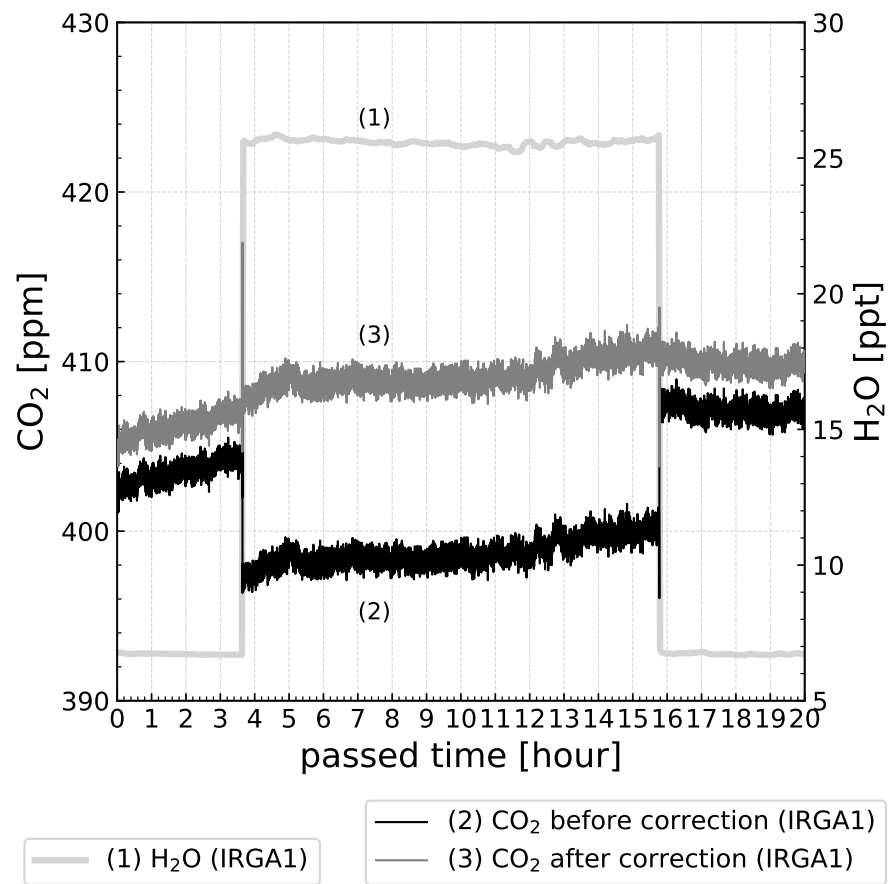


Figure C.7: Comparison between CO₂ concentration from IRGA1 before and after the correction using Eq.(S.C.45).

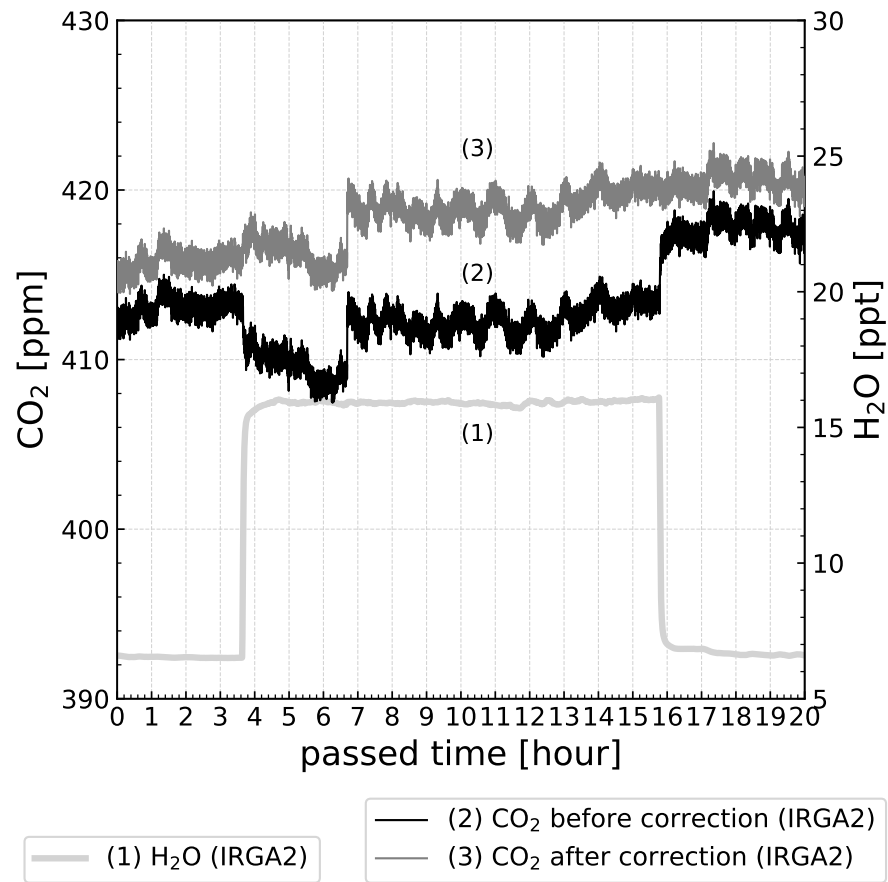


Figure C.8: Comparison between CO₂ concentration from IRGA2 before and after the correction using Eq.(S.C.45).

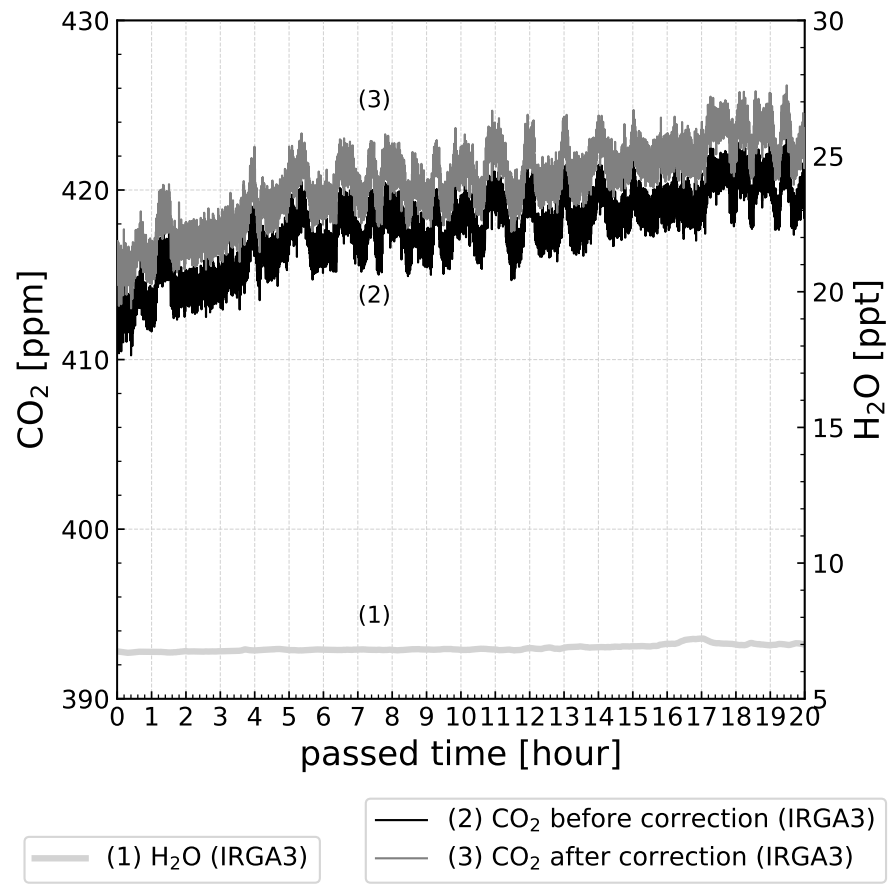


Figure C.9: Comparison between CO₂ concentration from IRGA3 before and after the correction using Eq.(S.C.45).

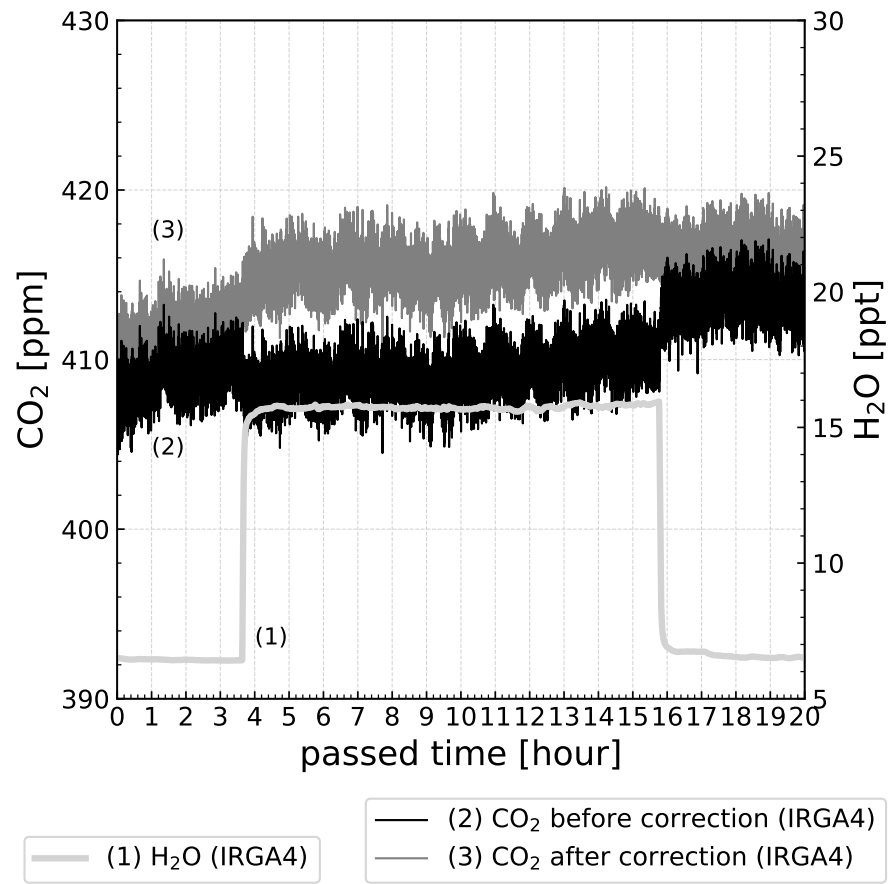


Figure C.10: Comparison between CO₂ concentration from IRGA4 before and after the correction using Eq.(S.C.45).