

Supplementary Material (ESI) for Reaction Chemistry & Engineering

Rapid CO₂ capture-to-mineralisation in scalable reactor

Ning Zhang^{1,2}, Rafael M. Santos^{2*}, Lidija Šiller^{1*}

¹ Newcastle University, School of Engineering, Newcastle upon Tyne, NE1 7RU, UK

² University of Guelph, School of Engineering, Guelph, Ontario, N1G 2W1, Canada

* Corresponding authors: santosr@uoguelph.ca; lidija.siller@ncl.ac.uk

Supplementary Information

The following sections provide further details on the modelling approach and the model calibration, present the modelling results, and discuss insights gained from the modelling that can be linked back to the experiments conducted. It is also discussed how the model can be used for further reactor optimization and reactor scale-up, and the possible impacts and improvements of the model assumptions.

S1. Pressure drop in tubular reactor

The viscosity and density of the liquid and gas phases are obtained from literature for different reaction temperatures.¹ With these properties, the Reynolds number ($Re=\rho Ud/\mu$) and Dean number ($De=Re(d/D)^{1/2}$) can be calculated, and used in the determination of the two-phase pressure drop of reactor. The tube diameter is d , and the curvature diameter of the helically coiled tube is D . The helical tubular reactor pressure drop is assumed to results from frictional resistance, and thus the two-phase pressure drop for the Taylor slug flow regime can be obtained by the Lockhart-Martinelli method.² The pressure drop multipliers, φ_G and φ_L representing two phase frictional multiplier for gas alone and flow two phase frictional multiplier for liquid alone flow, and the Lockhart-Martinelli parameter, χ , are defined with the following formulas:

$$\varphi_G^2 = \frac{(dp/dz)_{TP}}{(dp/dz)_G} \quad (E1)$$

$$\varphi_L^2 = \frac{(dp/dz)_{TP}}{(dp/dz)_L} \quad (E2)$$

$$\chi^2 = \frac{(dp/dz)_L}{(dp/dz)_G} \quad (E3)$$

The two phase pressure gradient is $(dp/dz)_{TP}$. The single phase pressure gradients above from the gas side as $(dp/dz)_G$ and from the liquid side $(dp/dz)_L$, which are determined assuming that each phase flows in the helicoid tubing alone (i.e. using the superficial velocity of each phase), are determined using the following equations:

$$(dp/dz)_G = \frac{2f_G \rho_G U_G^2}{d} \quad (E4)$$

$$(dp/dz)_L = \frac{2f_L \rho_L U_L^2}{d} \quad (E5)$$

μ , ρ and U is the viscosity, the density and the superficial velocity of the fluid in the gas and liquid phase, respectively. The friction factor (f) for laminar flow in a helicoid tubing is obtained using the empirical correlation below:³

$$\frac{f}{f_s} = \left[\left(1 - \frac{0.18}{\left[1 + \left(\frac{35}{De} \right)^2 \right]^{1/2}} \right)^m + \left(1.0 + \frac{d}{3D} \right)^2 \left(\frac{De}{88.33} \right) \right]^{1/2} \quad (E6)$$

In Eq. (E6): d is the tubing inner diameter and D is the coil diameter, $f_s = 16/Re$, which is the friction factor for straight tube; when $De < 20$, $m=2$; when $20 < De < 40$, $m=1$, and for other De , m equals 0. In the present case, De is less than 20, so m used is 2. The overall speed of fluids is mild; therefore, the centrifugal force was not taken into consideration in the model.

The two-phase frictional pressure drop (from Eq. (E1)) is used to calculate the pressure drop at each time step interval of the model, when the modelled element consisting of a liquid plug and a gas bubble travels a certain distance, depending on the total flow rate (i.e. the sum of liquid and gas superficial flowrates). The total pressure drop across the reactor is then determined based on the number of time steps needed for the liquid plug and gas bubble (if still present) to reach the reactor outlet.

Fig. S1 shows the two-phase pressure drop along the length of reactor for three different gas flow rates, at constant liquid flow rate of 40 mL/min. The outlet pressure is modelled as the atmospheric pressure, since the reactor dispenses the flow to an open cup. The pressure decreases as the reactor length increases, and the slight non-linearity is a result of the change in size of the gas bubble, which occurs both due to mass transfer (i.e. a shrinking effect) and due to gas de-pressurization (i.e. an expanding effect). Since these two effects have opposite outcomes on bubble size, and thus two-phase flow velocity, the resulting pressure drop becomes somewhat linear. The total pressure drop, as expected and experimentally observed, is greater with the higher gas flow rates, given the greater friction experienced, especially by the liquid phase that is accelerated by the gas in the two-phase region.

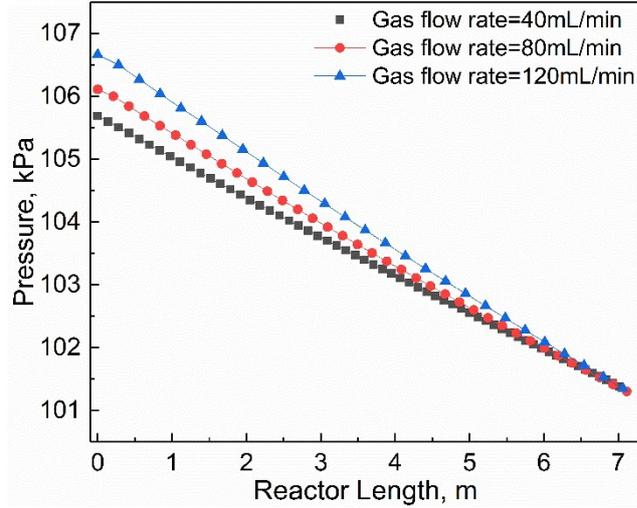


Fig. S1 Two-phase frictional pressure drop along with the reactor length with various gas flow rates, using 0.1 vol.% MEA solution and 40 mL/min liquid flow rate, at 50°C and 0.020 M Ca concentration in brine.

S2. CO₂ absorption in tubular reactor

To model the CO₂ absorption process (i.e. mass transfer from gas phase to liquid phase), the Two Film Theory based equations are applied.⁴ This film theory divides the liquid and gas phases into two bulk sources/sinks, and a permeable interface. Several assumptions need to be complied: (i) the liquid phase is well mixed (which is the case for liquid plugs moving in Taylor Flow regime), hence bulk gradients are negligible; (ii) the reactions of CO₂ in the liquid phase are fast, such that the liquid phase can reach the equilibrium rapidly; (iii) the driving force is determined by the CO₂ pressure difference between the gas and liquid phases (where the liquid phase concentration is converted into a pressure equivalent); (iv) the resistance of the interface to mass transfer is represented by a single overall resistance, meaning that boundary layers resistance, actual interface resistance, and any charge resistance are coupled into a single resistance.

In the case of the absorption process (without chemical reaction), the mass flux can be expressed by:

$$N_{CO_2} = K \left(P_{[CO_2]_i} - P_{[CO_2]_i}^* \right) \quad (E7)$$

where K is the overall mass transfer coefficient; $P_{[CO_2]_i}$ represents the pressure of the gas within the gas phase (i.e. bubble), and $P_{[CO_2]_i}^*$ is the pressure that is in equilibrium with the liquid phase concentration; hence the difference between these two pressures is the driving force of CO₂ absorption.

The obtained flux (N_{CO_2}) is multiplied by the duration of the time step to determine the change in concentration in the liquid phase during that time step, and subsequently, taking also into account bubble size and pressure drop, the change in mass and volume of the gas bubble during that time step. According to the Henry's Law, the equilibrium pressure can be obtained by the equation:

$$P_{CO_2}^* = C_{CO_2(L)}^*/H \quad (E8)$$

where H is Henry's Law constant; and $C_{CO_2(L)}^*$ is the concentration of dissolved (and unreacted) CO_2 in the liquid phase.

Henry's Law constant in the water can be calculated from the below equation;⁵ T^\ominus is 298.15K and all other parameters are obtained from the reference,⁵ $\Delta_{sol}H$ is the enthalpy of dissolution, thus the Henry's Law constant in water at 313.15K is 1.73E-04 mol/(m³.Pa).

$$H_{(T)} = H^\ominus \times \exp\left[\frac{-\Delta_{sol}H}{R}\left(\frac{1}{T} - \frac{1}{T^\ominus}\right)\right] \quad (E9)$$

This constant is accurate under water condition, and our experiments occurred in the presence of MEA solution, which means that in practice this pressure/concentration relationship requires a constant of higher value than that in water, due to higher solubility of CO_2 in MEA solution. On the other hand, aqueous MEA solution also influences the rates of absorption of CO_2 into solution, due to reactivity of CO_2 with MEA, increasing the mass transfer driving force. To account for these effects, a Henry's Law constant enhancement factor is introduced in the model, and the value is obtained from the literature based on the experimental temperature.⁶ In our case, the enhancement factor is adjusted to 2. Finally, these equations lead to determining the mass of dissolved CO_2 in the liquid plug (within the reactor element being modelled), before any chemical reaction occurs, which is then taken into account using equations in the next section.

S3. Chemical reactions in tubular reactor

Table S1. Chemical equilibrium constants used in the reaction model.

Species	Equilibrium constants	K value (313K)	Activity corrections	References
RNH_3^+	$K_1 = [RNH_3^+][OH^-]/[RNH_2]$	3.41E-05	K_1/γ_1^2	8
$RNHCOO^-$	$K_2 = [HCO_3^-][RNH_2]/[RNHCOO^-]$	6.47E-02	K_2	7
HCO_3^-	$K_a = [H^+][HCO_3^-]/[CO_{2(aq)}]$	5.01E-07	K_a/γ_1^2	9
CO_3^{2-}	$K_b = [H^+][CO_3^{2-}]/[HCO_3^-]$	6.00E-11	K_b/γ_2	9
$CaOH^+$	$K_3 = [CaOH^+][Ca^{2+}]/[OH^-]$	9.10E-02	$K_3 \times \gamma_2$	10
$CaHCO_3^+$	$K_4 = [CaHCO_3^+]/[Ca^{2+}][HCO_3^-]$	6.64E-02	$K_4 \times \gamma_2$	11
$CaCO_{3(s)}$	$K_{sp} = [Ca^{2+}][CO_3^{2-}]$	8.92E-09	K_{sp}/γ_2^2	12

Video 1. Gas and liquid mixed at T-junction with the flow ratio (L/G) at 40/40.

Video 2. The outlet bubble size in flow ratio (L/G) at 40/40.

Supplementary references

1. M.-J. Lee and T.-K. Lin, *Journal of Chemical & Engineering Data*, 1995, **40**, 336-339.
2. A. A. R. C. XIN, Z. F. DONG and M. A. EBADIAN, *Int. J. Heat Mass Transfer*, 1996, **39**, 735-743.
3. R. L. Manlapaz and S. W. Churchill, *Chemical Engineering Communications*, 1980, **7**, 57-78.
4. P. Danckwerts, *Industrial & Engineering Chemistry*, 1951, **43**, 1460-1467.
5. R. Sander, *Atmospheric Chemistry and Physics*, 2015, **15**, 4399-4981.
6. Y. Liu, L. Zhang and S. Watanasiri, *Industrial & Engineering Chemistry Research*, 1999, **38**, 2080-2090.
7. A. Aboudheir, P. Tontiwachwuthikul, A. Chakma and R. Idem, *Chemical Engineering Science*, 2003, **58**, 5195-5210.
8. R. G. Bates and G. D. Pinching, *Journal of Research of the National Bureau of Standards*, 1951, **46**, 349352.
9. J. T. Edwards, Maurer, G., Newman, J., Prausnitz, J.M., *A.I.Ch.E. Journal*, 1978, **24**, 966-976.
10. R. Bates, V. Bower, R. Canham and J. Prue, *Transactions of the Faraday Society*, 1959, **55**, 2062-2068.
11. R. L. J. a. D. Lanquair, *Geochimica et Cosmochimica*, 1974, **88**, 301-318.
12. L. N. Plummer and E. Busenberg, *Geochimica et cosmochimica acta*, 1982, **46**, 1011-1040.