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SIMPLE MODEL FOR CO_2 ABSORPTION IN A BUBBLING WATER COLUMN

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Abstract - A simple analytical model is presented for the time-evolution of dissolved CO_2 concentration in a batch water column. The application in mind is the removal of the CO_2 produced by the propulsion plant of a submarine cruising underwater. The model is based on a constant number of constant size CO_2 bubbles within the water column, with uniform gas injection through a porous membrane at the bottom, and bubbles flowing upwards by their own buoyancy through a short water column (the exhaust gas is recirculated). Analytical results are validated with experimental data found in the literature and the advantages of this simple analytical model pinpointed.

Keywords: Carbon dioxide water solutions; CO_2 absorption; Bubble column; Dissolution; Batch; Absorption.

INTRODUCTION

Hydrocarbon-oxygen-based propulsion systems on board submarines generate great quantities of water and CO_2 during operation; the latter cannot be stored aboard and must be expelled to outside seawater under submerged condition. Among the several options to remove CO_2 from submarines cruising underwater (see Potter *et al*., 2000), the one selected here is to dissolve the gas in seawater in batch at low pressure in a bubble column (inside the submarine) and then to pump the water outside, aided by a work exchanger device to minimize pumping power.

Bubble generation is by the flow of gas through a porous membrane at the bottom of the water column, while buoyancy provides the bubble dispersion mechanism that enhances the gas absorption rate. Undissolved gas is collected at the top and recirculated.

Mean bubble radius, r_0, is governed by two basic phenomena (Parthasarathy *et al*., 1996, Ribeiro *et al*., 2004):

- Surface coalescence at the porous membrane before the bubble detaches. When the membrane pore size becomes small enough, $d \ll 10^{-4}$ m, it appears that the size of the bubbles formed on the membrane tends to stabilize around a limiting value approximately equal to $r_0=0.19$ mm (Parthasarathy *et al*., 1996).
- Flow coalescence of bubbles in the bulk. For large gas injection speeds, $u_g>0.1$ m/s, collisions between bubbles in the bulk water favor the formation of bubbles larger than when detached from the membrane surface (Moshtari *et al*., 2009) and the flow regime changes from homogeneous to heterogeneous. Flow coalescence increases with bubble number density (n/V).

The model developed here assumes that there is no flow coalescence ($u_g \ll 0.1$ m/s), and is intended

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*To whom correspondence should be addressed to be applicable to small bubbles of any size (assumed spherical; in the range r_0=0.1 mm to 0.5 mm), although our interest is in small sizes, to maximize absorption rate (for the submarine application one has to dispose of at least 0.05 kg/s of CO_2, in a tightly constrained engine room). In spite of the many simplifications introduced into the model (uniform constant bubble radius, constant pressure, pure gas, pure water, no chemical reactions…), its predictions compare favourably with more sophisticated analytical and experimental results.

MATHEMATICAL MODEL OF ABSORPTION RATE

The diffusion mass flux j_g of a dissolved gas in a liquid of density ρ_l, gas mass fraction w, and gas diffusivity D_g, in spherical coordinates, assuming spherical symmetry, is (Fick's law):

$$j_g = \frac{\dot{m}_c}{4\pi r^2} = -D_g \frac{d\left(w\rho_l\right)}{dr} \tag{1}$$

Integration in r from the bubble radius r_0 to infinity, and application of mass balance of the gas (pure-CO_2), of density $\rho_g = p_g/(R_g T)$, assuming time independence and constant liquid density, as in Darmana *et al.* (2004), yields a simple expression for the total dissolution time, t_d:

$$\left.\begin{array}{l} \dfrac{\dot{m}_{g0}}{4\pi r_0} = D_g \rho_l \left(w_0 - w_\infty\right) \\ \dot{m}_{g0} = \dfrac{d\left(\frac{4}{3}\pi r_0^3 \rho_g\right)}{dt} \end{array}\right\} t_d = \frac{\rho_g r_0^2}{2 D_g \rho_l \left(w_0 - w_\infty\right)} \tag{2}$$

Because we deal with short columns, we assume that the residence time of the bubbles in the column, $t_r = L/u_b$, is much smaller than the total dissolution time, t_d, and hence there is a nearly constant bubble radius along the column, since only a small amount of gas dissolves in one pass. The short-column approach also justifies the assumption of constant gas density along the column (small change in hydrostatic pressure). Besides, capillary overpressure inside the bubble is also neglected, because only radii r_0>0.1 mm are envisaged, as explained above).

The bubble rising speed, u_b (terminal velocity) is determined by the buoyancy/friction matching, the first being the weight of liquid displaced by the bubble and the latter being the drag on a sphere given by Stoke's law for low Reynolds number flows (Re<10):

$$F = \frac{4}{3}\pi r_0^3 \rho_l g = 6\pi \mu_l r_0 u_b \quad \rightarrow \quad u_b = \frac{2g}{9\nu_l} r_0^2 \tag{3}$$

with g=9.8 m/s^2, and μ_l and ν_l being the dynamic and kinematic viscosities of the liquid. The time it takes for a detaching bubble to reach terminal speed is really negligible.

The number of bubbles, n, in a liquid column of height L and cross-sectional area A depends on feeding rate, measured by the gas injection speed at the bottom, u_g, and on bubble size r_0, as computed by the product of number of bubbles injected per unit time, $\dot{n}$ (the volumetric flow rate is $u_g A$), times the residence time of bubbles in the column, $t_r = L/u_b$:

$$n = \dot{n} t_r = \frac{A u_g}{\frac{4}{3}\pi r_0^3} \frac{L}{u_b} = \frac{27 \nu_l L A u_g}{8\pi g r_0^5} \tag{4}$$

Gas diffusion from bubbles to liquid increases the solute concentration, measured by its mass fraction far from the bubble surface, w_∞. The dissolving rate equation for the whole column is obtained from the solute mass balance:

$$\begin{aligned} & AL\frac{d\left(w_\infty \rho_l\right)}{dr} = \dot{m}_{g0} n = \\ & = 4\pi r_0 D_g \rho_l \left(w_0 - w_\infty\right) \frac{27 \nu_l L \dot{m}_g}{8\pi g \rho_g r_0^5} \\ & \rightarrow \frac{dw_\infty}{dt} = \frac{27 \nu_l D_g u_g}{2 g r_0^4}\left(w_0 - w_\infty\right) \end{aligned} \tag{5}$$

Integrating Eq. (5) from w_∞=0 at t=0 to a desired mass-fraction before venting, w_∞, one gets the time-evolution for w:

$$\begin{aligned} & w_\infty\left(t_v\right) = w_0\left[1 - \exp\left(-K t_v\right)\right], \text{ with} \\ & K \equiv \frac{27 \nu_l D_g u_g}{2 g r_0^4} \end{aligned} \tag{6}$$

For a given gas injection speed, u_g, and bubble radius, r_0, Eq. (6) allows one to find an appropriate venting time, t_v, to get rid of the CO_2-loaded batch water, before the bath gets near saturation and the mass transfer rate becomes impossible. The advantage of this simple analytical model is that the influence of the different controlling parameters is explicit in Eq. (6); i.e., we see that the required area (or the venting time) is proportional to the fourth power of r_0, and inversely proportional to u_g.

VALIDATION OF RESULTS

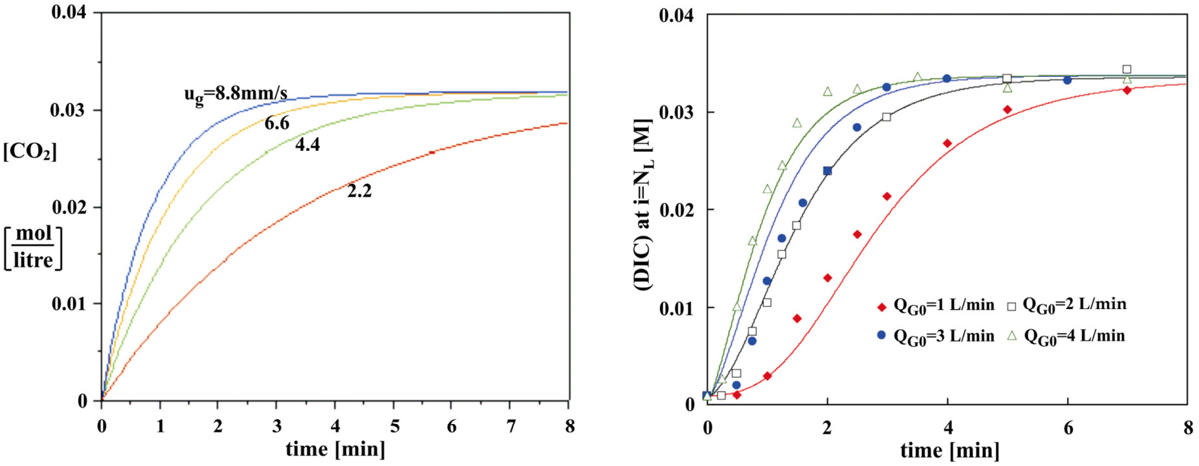
Experimental data presented in Parthasarathy *et al*. (1996) show that there is a minimum bubble radius (about r_{0min}=0.19 mm) attainable when injecting a gas through a porous membrane into a liquid, due to bubble coalescence at the interface before the bubble detaches.

Tokumura *et al*. (2007) present an involved theoretical model of the dynamics of CO_2 absorption in water (including different species in solution and chemical reactions), and supporting experimental data. In particular, they show the effect of several gas injection rates (Q_{G0}=1 L/min to Q_{G0}=4 L/min in their Fig. 3b, included here), in the time-evolution of CO_2 molar concentration (their dissolved inorganic carbon-dioxide-equivalent molarity, DIC), for a cross-sectional area A=75.4 cm^2. When we plot our result Eq. (6) in terms of molar concentration, $DIC=w_s\rho_l/M_g$, for the corresponding injection speeds $u_g=Q_{G0}/A$ (2.2 mm/s to 8.8 mm/s), and the property values for their conditions (24ºC and 100 kPa, $w_0=pS/\rho_l=(10^5)(2\times10^{-5})/10^3=0.002$), we get Fig. 1a.

We can see from Fig. 1 that the behaviour for large injection rates is fully predicted: the water becomes nearly saturated in a couple of minutes (the small differences in saturation values are just due to typical uncertainties in material-property data). Our model is not so good for small injection rates because, in this case dissolution and residence times are of the same order of magnitude, which means that, at least in the initial stage of the process, bubbles completely dissolve before reaching the top of the column, invalidating our assumption of constant bubble radius. For large injection rates, however, the CO_2 mass-fraction in the water column, w_∞, increases rapidly, and bubble dissolution time also increases quickly by reduction of w_0-w_∞ in Eq. (2), with the consequence that the radius of bubbles detached from the membrane has a practically constant value during most of the absorption process.

With this assurance of the validity of our model Eq. (6) for high gas injection speeds (u_g>4 mm/s) and minimum bubble radius (r_0=0.19 mm), it is easy to make preliminary design calculations, as presented now for our application to CO_2 removal in air-independent submarine propulsion.

We approximate seawater properties by typical plain water values: density ρ_l=1000 kg/m^3, kinematic viscosity $\nu_l=10^{-6}$ m^2/s; we take $D_g=2.1\times10^{-9}$ m^2/s for CO_2 diffusion in water; gas density at working conditions $\rho_g=p_g/(R_gT)=2\times10^5/(189\cdot288)=3.7$ kg/m^3, since absorber operation is expected at a constant pressure p=200 kPa. The saturation mass fraction at this pressure is $w_0=pS/\rho_l=(2\times10^5)(2\times10^{-5})/10^3=0.004$ (4 g of CO_2 per kg of solution, i.e., a molar concentration $c_0=w_0\rho_l/M_g=(0.004)(1000)/0.044=91$ mol/m^3), where $S=2.0\times10^{-5}$ kg/(m$^3\cdot$Pa) is the solubility of CO_2 in water at 15ºC (Carrol *et al*. 1991).



(a) (b)

Figure 1: Effect of CO_2 gas injection speed on CO_2 absorption at 24ºC in plain water; a) according to Eq. (6); b) according to Tokumura *et al*. (2007).

We choose as design parameters for our submarine application to remove $\dot{m}_{CO_2}$=0.05 kg/s (the CO_2 produced by a 200 kW engine), a water column of L=0.50 m in height, and a gas injection speed of u_g=10 mm/s. Assuming a mean bubble radius of r_0=0.19 mm (the experimental limit of Parthasarathy *et al.*, 1996), in the limit of pure water (w_∞=0) we have:

- Bubble dissolution time, from Eq. (2), is t_d=7.9 s.
- Bubble rising speed, from Eq. (3), is u_b=0.080 m/s. It would take then a distance of $L=u_bt_d$=(0.08)(8)=0.64 m for a bubble to fully dissolve. The Reynolds number is $Re=2u_br_0/\nu_l$=30, above the Stokes law limit in Eq. (3), but its effect must compensate somehow in view of the good experimental agreement in Fig. 1. It can be further shown that the mean distance between bubble centres is 0.61 mm, and the mass-transfer area density $a=4\pi r_0^2n/V$=2000 m^2/m^3.
- Bubble residence time is $t_r=L/u_b$=0.5/0.080=6.2 s. Note that the radius decreases only 47% in spite of $t_r/t_d\approx$78% because it is the bubble area which decreases linearly with time, as can be seen in Eq. (2).
- Mass-fraction of CO_2 in the column after venting time t_v is, from Eq. (6), $w_v=0.004(1-\exp(-Kt_v))$, with K=0.022 s^{-1}, so that, if we scavenge when the water becomes half-saturated (w_v=0.002), then the venting time is t_v=ln2/K=31 s.
- Required column cross-section area, A, to get rid of $\dot{m}_{CO_2}$=0.05 kg/s:

$$A=\frac{\dot{m}_{CO_2}t_s}{w_v\rho_lL}=\frac{0.05\cdot 31}{0.002\cdot 1000\cdot 0.5}=1.5\ m^2 \qquad (7)$$

which seems reasonable to be accommodated within a submarine engine room, although a smaller size would be preferable. To make the batch processing smoother and to enhance redundancy, 4 o 6 small and slender cylinders could be used to distribute that cross-sectional area.

CONCLUSIONS

A simple analytical model has been developed here to predict the time-evolution of CO_2 absorption in water. This model clearly shows the effects of several parameters that influence the absorption rate: bubble size, injection rate, or temperature (through the change in material properties). Although our final goal was to have a simple formulation of the absorption rate, to be integrated in a larger numerical simulation of the whole CO_2 removal system for a conventional submarine with air-independent propulsion, we believe that it can be of interest in many other applications within the stated assumptions (relatively large gas injection speeds, small bubble size, and relatively short batch water columns).

NOMENCLATURE

A	Area of cross-section	m^2
D_g	Diffusion coefficient of CO_2 gas in water	m^2/s
d	Membrane pore size	m
F	Drag	N
g	Gravity acceleration	m/s^2
j	Mass flow per unit surface	$(kg/s)/m^2$
K	Mass transport coefficient	1/s
L	Bubble column height	m
$\dot{m}$	Mass flow rate	kg/s
n	Amount of substance	mol
$\dot{n}$	Molar flow rate	mol/s
p	Pressure	Pa
R	Gas constant	$J/(kg\cdot K)$
r_0	Bubble radius	m
r	Radial coordinate	m
S	Solubility of gas in liquid	$kg/(m^3\cdot Pa)$
T	Temperature	K
t	Time	s
u	Velocity	m/s
V	Volume	m^3
w	Mass fraction	

Greek Letters

ρ	Density	kg/m^3
μ	Dynamic viscosity of liquid	$Pa\cdot s$
ν	Kinematic viscosity of liquid	m^2/s

Subscripts

b	Bubble
c	CO_2
d	Dissolving
g	Gas (bubbles)
l	Liquid
r	Residence
v	Venting
0	At the liquid/gas interface
∞	Far from the liquid/gas interface

REFERENCES

Carroll, J. J., Slupsky, J. D., Mather, A. E., The solubility of carbon dioxide in water at low pressure. Journal of Physical and Chemical Ref. Data, 20, (6), pp. 1201-1209 (1991).

Darmana, D., Deen, N. G., Kuipers, J. A. M., Modelling of mass transfer and chemical reactions in bubble column reactor using a discrete bubble model. Fifth International Conference on Multiphase Flow, Yokohama, Japan (2004).

Moshtari, B., Babakhani, E. G., Moghaddas, J. S., Experimental study of gas hold-up and bubble behavior in gas-liquid bubble column. Petroleum & Coal, 51, (1), pp. 27-32 (2009).

Parthasarathy, R., Ahmed, N., Size distribution of bubbles generated by fine-pore spargers. Journal of Chemical Engineering of Japan, 29, (6), pp. 1030-1034 (1996).

Potter, I. J., Clavelle, E., Reader, G. T., Kady, J., Carl, M., Exhaust gas management systems for underwater heat engines. In Proceedings of the 2000 International Symposium on Underwater Technology, (Cat. No.00EX418) (2000).

Ribeiro, C. P., Lage, P. L. C., Experimental study of bubble size distributions in a direct-contact evaporator. Brazilian Journal of Chemical Engineering, 21, (1), pp. 69-81 (2004).

Tokumura, M., Baba, M., Kawase, Y., Dynamic modeling and simulation of absorption of carbon dioxide into sea water. Chemical Engineering Science, 62, pp. 7305-7311 (2007).