

GHGT-11

Ex-situ dissolution of CO₂ for carbon sequestration

Aleksander Cholewinski^a and Yuri Leonenko^{a*}

^a*Department of Physics, University of Waterloo, Waterloo, Ontario, N2L 3G1, Canada*

Abstract

In this paper, a model for diffusion-controlled dissolution of CO₂ droplets during co-current (CO₂-brine) horizontal turbulent pipe flow is presented. The objective is to evaluate the feasibility of ex-situ dissolution of CO₂ before it is injected underground. Potential maximum droplet sizes for CO₂ droplets are calculated, and compared with an estimated inner scale of turbulence. A comparison is made between times to dissolve for turbulent and diffusion dissolution, as well as an estimation of required pipe length needed for purely diffusion-based dissolution.

© 2013 The Authors. Published by Elsevier Ltd.
Selection and/or peer-review under responsibility of GHGT

Keywords: ex-situ dissolution; aquifer; CO₂ sequestration

1. Introduction

Assessments reported by the Intergovernmental Panel on Climate Change [1] conclude that CCS (Carbon Capture and Storage) could play a major role in mitigating climate change associated with CO₂ emissions. Pilot and industrial scale of CCS projects provide strong empirical support for the view that CO₂ storage can be implemented safely. Nevertheless, significant uncertainties remain regarding the security of underground storage. The major technical concern is the risks of leakage. Since CO₂ injected into deep underground formations is typically less dense than the resident fluids, it may flow upwards leaking through any high permeability zones or artificial penetrations such as wells.

Therefore, a critical issue for geological storage is to ensure that the stored CO₂ does not escape from the underground formations. Development of methods and tools to mitigate the risks of leakage provide great benefits for widespread of CO₂ storage technologies, facilitating regulatory and policy decisions.

In conventional approach, after injection CO₂ will slowly dissolve in aquifer brine. The time needed for the CO₂ to dissolve completely depends on reservoir conditions and typically is on the order of thousands years [2,3]. Previously [4], it was shown that it is possible to accelerate the dissolution process by pumping brine from regions where it is undersaturated into regions occupied by CO₂. Such active

* Corresponding author. Tel: +1 (519) 888-4567 (Ex. 32160); Fax: +1 (519) 746-8115;
E-mail: leonenko@uwaterloo.ca

engineering could reduce dissolution time to hundreds of years. In the same paper a surface (or ex-situ) dissolution which could be achieved within a surface pipeline was suggested, aiming CO_2 to be dissolved before it is injected underground. In the study presented here a feasibility of this idea, as seen in Figure 1, is investigated in detail.

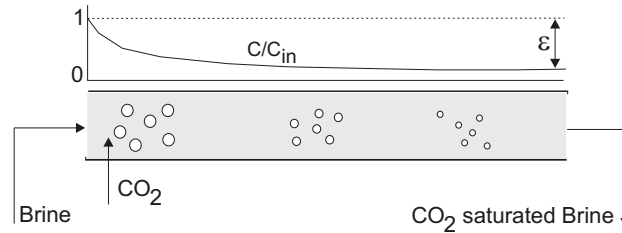


Figure 1 CO_2 dissolution in brine as it travels through a pipe.

In this approach brine produced from target aquifer is mixed with previously captured and liquefied carbon dioxide. After that carbon dioxide-brine mixture enters a pipe where the process of dissolution of carbon dioxide in brine occurs. After the dissolution process is completed in the pipe, CO_2 saturated brine is injected back to the aquifer. Varieties of two phase pipe flow regimes are possible depending on brine and CO_2 flow rates and properties, but since the solubility of carbon dioxide is low complete dissolution will require low CO_2 hold ups during the process. This constraint along with a high (overall) mixture loads (flow velocities) will result in turbulent droplet flow which is the most effective regime for mass transfer (dissolution).

In our previous work [5] a turbulent mass transfer from CO_2 droplets into brine during co-current (CO_2 -brine) horizontal pipe flow was investigated to evaluate the feasibility of the proposed method. The model development was based on [6] considering mass transfer from cloud of droplets with a given hold up.

The dissolution efficiency, ϵ , shown in Figure 1 depends on multiple parameters such as flow rates and pipe diameter. These parameters control turbulence intensity and as a result, control the coefficient of mass transfer as well as initial (inlet) droplets size. Different flow rates, pipe diameters, CO_2 hold ups, correlations for coefficient of turbulent mass transfer had been investigated [5]. The results are very promising showing fast dissolution in the case of turbulent regime but when droplets size reaches scales comparable to inner scale of turbulence one should consider diffusive mass transfer in the cloud of droplets (even though flow is turbulent overall).

We showed that diffusive mass transfer rates are much slower comparing to turbulent ones, but since droplets are small when diffusive mechanism starts to govern the process, the overall time for complete dissolution is reasonably small.

When compared with direct underground disposal, where the density of CO_2 is less than the density of residual fluid already in the underground formation, the present approach has the following benefits:

- eliminates the risk of CO_2 leakage to the surface;
- expands the range of underground formations suitable for disposal;
- simplifies risk management of disposal projects and makes them more cost efficient

2. Diffusion Dissolution Model

In order to examine dissolution rates below the inner scale of turbulence, as well as provide a comparison to the turbulent dissolution examined in [5], this paper investigates purely diffusion-based dissolution. The diffusion equation to describe this system (of a sphere of pure component A dissolving in a liquid medium of component B) is provided by Readey and Copper [7] to be, in the dimensionless form:

$$\frac{\partial c}{\partial \tau} - \left[\frac{2}{r^*} - (1 - \alpha) \frac{a^{*2}}{r^{*2}} \frac{da^*}{d\tau} \right] \frac{\partial c}{\partial r^*} - \frac{\partial^2 c}{\partial r^{*2}} = 0, \quad (1)$$

with

$$\frac{da^*}{d\tau} = \beta \left(\frac{\partial c}{\partial r^*} \right)_{r^*=a^*}. \quad (2)$$

In these equations, the dimensionless form for each term can be acquired through the following transformations:

$$c = \frac{C - C_\infty}{C_a - C_\infty}, \quad \tau = \frac{Dt}{a_0^2}, \quad r^* = \frac{r}{a_0}, \quad a^* = \frac{a}{a_0}. \quad (3)$$

Here, ρ is the concentration, r is the radial distance from the center of the droplet, t is time, a is the radius of the droplet (with a_0 being the radius at time $t = 0$), C_∞ is the initial concentration of component A in the medium, C_a is the concentration of A at the surface of the sphere, and D is the diffusion coefficient of A in B. Additionally, the parameters α and β are defined as

$$\alpha = C_s \bar{V}_A, \quad (4)$$

$$\beta = \frac{C_a - C_\infty}{C_s(1 - C_a \bar{V}_A)}, \quad (5)$$

where c_s is the droplet density and \bar{V}_A is the partial molar volume of A in B. α is the ratio between the volume A occupies in B and the volume of A in the droplet. As such, when $\alpha = 1$, there is no density change of component A on mixing, resulting in no bulk radial flow of the liquid, and when $\alpha = 0$, the density of the solution is independent of the concentration of A in the solution [8].

The boundary and initial conditions for this problem are given as

$$\begin{aligned} c(r, t) &= c_a, & r^* &= a^*, \tau > 0 \\ c(r, t) &= c_\infty, & r &> a_0^*, \tau = 0 \\ c(r, t) &= c_s, & r &< a^*, \tau \geq 0 \\ a^*(t) &= a_0^*, & \tau &= 0. \end{aligned} \quad (6)$$

There is one additional boundary condition, defining the concentration far away from the droplet. Originally, the assumption made was that of a single droplet in an infinite liquid [8]. However, in the conditions given in this paper, it becomes important to consider the contribution of other droplets. Similarly to [4,5], this paper accounts for the presence of other droplets in the solution using a simple cell model, where each droplet is considered to be inside an isolated cell (with size dependent on the volume fraction of droplets in the liquid, ϕ), with the assumption that there is no mass transfer at the boundary, as

mass transfer between cells is assumed to be in equilibrium. The radius of the cell, R , can be found from the volume fraction

$$\frac{a^3}{R^3} = \phi, \quad R^* = \frac{R}{a_0}. \quad (7)$$

The assumption of no mass transfer at the cell boundary becomes the final boundary condition:

$$\frac{\partial c}{\partial r^*} = 0, \quad r^* = R^*, \tau \geq 0. \quad (8)$$

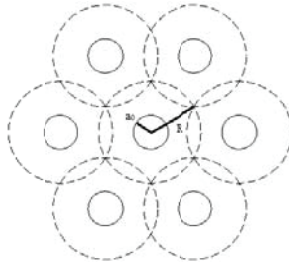


Figure 2 CO₂ droplet in a cell of neighbours.

2.1. Additional Assumptions

In order to simplify the calculations, several assumptions have been made about the system. The first assumption is that the effects of surface tension are negligible. As shown by Karabelas, in the case of a dissolving bubble, surface tension has the effect of speeding up the rate of dissolution. This makes sense, as surface tension would provide a force pulling inward on the droplet, causing it to shrink more quickly. As one goal of this paper is to provide an estimate for the longest time possible (worst case scenario) a droplet would take to fully dissolve, the inclusion of surface tension was not considered. Another effect not covered by this paper is the possibility of formation of a CO₂ hydrate. While this would change the mechanics and rate of dissolution, Ng & Robinson show that CO₂ hydrates only form at temperatures below ~12°C, and then at very high pressures [9]. Since the conditions we are using cover lower pressures and a higher temperature, any effects of CO₂ hydrate formation can be neglected.

2.2. Droplet Size

In order to have a reasonable idea of the time of dissolution for a droplet, as opposed to simply knowing the dimensionless time, the initial droplet size is a necessary parameter. To see the longest time taken to dissolve, the maximum droplet size, d_{\max} , was of particular interest. Several equations have been developed in order to predict this maximum droplet size in turbulent pipe flow, such as those by Hesketh et al. [10], Karabelas [11], and Angeli and Hewitt [12].

Hesketh et al. provided an equation for d_{max} based on theory suggested by Levich. This equation uses properties of both the continuous and dispersed phases – brine and CO₂ droplets, respectively, in this case – as well as the critical Weber number of Levich's theory, We'_{crit} , to calculate d_{max} as

$$d_{max} = 1.38(We'_{crit})^{0.6} \left(\frac{\sigma^{0.6}}{\rho_c^{0.3} \rho_d^{0.2} \mu_c^{0.1}} \right) \left(\frac{D^{0.5}}{U^{1.1}} \right), \quad (9)$$

Where σ is the interfacial surface tension, ρ is the density, D is the pipe diameter, U is the average flow velocity, and the subscripts c and d denote the continuous and dispersed phases, respectively.

Another equation for maximum droplet diameter is provided by Karabelas, based on that of Hinze, and is used to calculate d_{95} , which is the droplet diameter for which 95% of the total volume of droplets are equal to or smaller in size. This equation states that

$$\frac{d_{95}}{D} = 1.516 \left[\frac{\sigma}{D \rho_c U^2} \right]^{0.6} Re^{0.10}. \quad (10)$$

In an attempt to better match experimental data, Karabelas suggests another equation for d_{95} . This equation is slightly simpler than that of Hesketh et al., and gives

$$\frac{d_{95}}{D} = 4.0 We^{-0.6}, \quad (11)$$

where We is a dimensionless Weber number used for this equation, dependent of pipe diameter and velocity, and is defined as

$$We = \frac{D \rho_c U^2}{\sigma}. \quad (12)$$

Additionally, there is another equation to calculate d_{max} , provided by Angeli and Hewitt, which states that

$$\left(\frac{d_{max} \rho_c v_c^2}{\sigma} \right) \left(\frac{f d_{max}}{4D} \right)^{\frac{2}{3}} = 0.369, \quad (13)$$

where f is the friction factor, provided by Churchill [13] to be

$$f = \left(\left(\frac{8}{Re} \right)^{12} + (A + B)^{-\frac{3}{2}} \right)^{\frac{1}{12}}, \quad (14)$$

with parameters A and B defined as

$$A = \left[-2 \log \left(\frac{(Ro)}{3.7} + \left(\frac{7}{Re} \right)^{0.9} \right) \right]^{16}, \quad (15)$$

$$B = \left(\frac{37530}{Re} \right)^{16}.$$

Ro is the roughness of the pipe, and $Re = \frac{UD}{\nu}$ is the Reynolds number based on pipe diameter, with ν the kinematic viscosity of the continuous phase.

Table 1 Parameters used for the system of turbulent flow CO₂ droplets in brine within a horizontal pipe (the same used in [5]).

Parameter	Value
D (m)	0.15
U (m/s)	1.81
ρ_c (kg/m ³)	1029
ρ_a (kg/m ³)	810
μ_c (mPa s)	1.08
ν (m ² /s)	1.050×10^{-6}
σ (mN/m)	33
ϕ	0.05
Ro (m)	45×10^{-6}
Re	259000

2.3. Inner Turbulence Scale

While assuming a droplet undergoes diffusion-controlled dissolution from its initial size gives the most conservative estimates of dissolution time, most droplets are large enough that they begin within the turbulent regime. Townsend, as well as Kawase et al., proposed that the inner turbulence scale, I , which gives a rough estimate of the boundary of droplet size between the turbulent and diffusive regimes, could be estimated by

$$I \propto 5.3D Re^{-\frac{3}{4}}. \quad (16)$$

Since the exact value of I is unknown, and since it is not a hard boundary between the two regimes, it was of interest to gain a stronger understanding of how close in size a droplet could become, while still undergoing turbulence-controlled dissolution. Kress and Keyes [14] provided experimental data that could help narrow down the range for I , as they used differing droplet sizes in varying Reynolds numbers, all of which remained within the turbulent regime. This data can be used to provide a better idea of an upper bound for I through the smallest droplet size still under turbulent conditions. Also, it is important to note that the parameter given for droplet size was the Sauter mean diameter, d_{32} , as opposed to d_{max} . This gives more useful information, as opposed to using d_{max} , when comparing the smallest size value to that of I .

The values examined were taken from Figure 5 in Kress and Keyes [14], which provides purely horizontal flow data, and is not noted to have atypical behaviour. Based on the pipe diameter of 2.0 in. and Re ranging from 20000 to 50000, I becomes proportional to values between 0.081 mm and 0.160

mm. It is this upper value of 0.160 mm that is of interest in comparison with the droplet sizes. The given values of d_{32} start at 0.381 mm and go up to 1.016 mm. Comparing the smallest value of d_{32} , 0.381 mm, to the largest value of I , 0.160 mm, shows that the droplet remains in the turbulent regime at a size ~ 2.4 times the value of I . This provides a reasonable upper limit for I that will be used when calculating its value for the case of CO₂ droplets dissolving in brine.

3. Results and Discussion

Using methods detailed earlier, the d_{max} or d_{95} values were calculated from the parameters in Table 1. Then, the time to complete droplet dissolution, t_d , was calculated for these varying diameters using Equation (1), with results for d_{max} , d_{95} , and t_d shown in Table 2. Working with the value of U from Table 1, this means that the largest droplets would need a pipe 10-65 km long (based on the value of d_{max}) to completely dissolve all injected CO₂ droplets.

Table 2 Calculated values for d_{max} using equations from various sources and inner scale of turbulence

Equation used	Diameter Parameter	Value (mm)	t_d (s)
Equation (9)	d_{max}	2.5	3.6×10^4
Equation (10)	d_{95}	2.4	3.5×10^4
Equation (11)	d_{95}	1.8	2.0×10^4
Equation (13)	d_{max}	1.0	5.6×10^3
Inner scale	I	0.17	160

In order to compare the time spent by a droplet in turbulent as opposed to diffusive mass transfer dissolution, a value for I is also needed. From Equation (16),

$$I \propto 0.069 \text{ mm}. \quad (17)$$

Scaling this value of I by 2.4 times gives an approximate upper bound for I of 0.17 mm. Comparing this to the smallest d_{max} value from Table 2, from Equation (13), it can be seen that the value of d_{max} is ~ 5.9 times that of I . Since these are diameter values, the maximum droplet volume, then, is ~ 200 times that of a droplet with a diameter of 0.17 mm. As such, the largest droplets will likely remain under turbulent diffusion until they are about 0.5% their original size. While this is specifically for the largest droplets in the distribution, it still gives some idea about the percentage of dissolution that is dominated by diffusion.

Additionally, t_d was calculated for this upper bound value of I , to see time taken to dissolution once a droplet reaches this scale. t_d for this case was found to be 161.7 s. This time, however, is calculated based on the assumption that the droplet starts at this size, with $a_0 = 0.17 \text{ mm}$ (Table 2). Since the droplet surface is assumed to be stationary at $t = 0$, and since the motion of the surface inwards increases rate of dissolution, t_d for this case is larger than it would actually be for a droplet that is shrinking past I . In comparison to the time for diffusion dissolution from I , droplets in the same conditions were predicted to take 200-800 s with turbulent dissolution [5]. As such, adding the time taken by turbulent dissolution to the t_d value from starting at I gives a total time in a range ~ 400 -1000 s. With an upper limit of ~ 1000 s, this would result in requiring a pipe with a length of about 2 km.

A droplet undergoing purely diffusion-based dissolution will dissolve much more slowly than one that experiences turbulent dissolution. However, while a dissolving droplet in turbulent flow will switch from

turbulent dissolution to diffusion dissolution in the region of the inner scale of turbulence, the size at which this change occurs is much smaller than the initial droplet size. As such, under the conditions in Table 1, diffusion is only responsible for the dissolution of a very small fraction of the original droplet's size, but due to very slow diffusive rates, the time scales and pipe lengths are the same order of magnitudes for both regimes, so both need to be taken into account.

References

- [1] Intergovernmental Panel on Climate Change: Special Report on Carbon Dioxide Capture and Storage, 2005. <http://www.ipcc.ch/pub/reports.htm>
- [2] Hassanzadeh H, Pooladi-Darvish M, Keith DW. Stability of a fluid in a horizontal saturated porous layer: effect of non-linear concentration profile, initial, and boundary conditions. *Transport in Porous Media* 2006;65:193–211.
- [3] Riaz A, Hesse M, Tchelepi HA, Orr FM. Onset of convection in a gravitationally unstable diffusive boundary layer in porous media. *Journal of Fluid Mechanics* 2006;548:87.
- [4] Leoneko Y, Keith DW. Reservoir Engineering To Accelerate the Dissolution of CO₂ Stored in Aquifers. *Environmental Science & Technology* 2008;42:2742–7.
- [5] Zendejboudi S, Khan A, Carlisle S, Leoneko Y. Ex Situ Dissolution of CO₂ : A New Engineering Methodology Based on Mass-Transfer Perspective for Enhancement of CO₂ Sequestration. *Energy & Fuels* 2011;25:3323–33.
- [6] Lezhnin S, Eskin D, Leoneko Y, Vinogradov O. Dissolution of air bubbles in a turbulent water pipeline flow 2003;39:483–7.
- [7] Readey DW, Copper AR. Molecular diffusion with a moving boundary and spherical symmetry. *Chemical Engineering Science* 1966;21:917–22.
- [8] Cable M, Evans DJ. Spherically Symmetrical Diffusion-Controlled Growth or Dissolution of a Sphere. *Journal of Applied Physics* 1967;38:2899–906.
- [9] Ng H-J, Robinson DB. Hydrate formation in systems containing methane, ethane, propane, carbon dioxide or hydrogen sulfide in the presence of methanol. *Fluid Phase Equilibria* 1985;21:145–55.
- [10] Hesketh RP, Fraser Russell TW, Etschells a. W. Bubble size in horizontal pipelines. *AIChE Journal* 1987;33:663–7.
- [11] Karabelas a. J. Droplet size spectra generated in turbulent pipe flow of dilute liquid/liquid dispersions. *AIChE Journal* 1978;24:170–80.
- [12] Angeli P, Hewitt GF. Drop size distributions in horizontal oil-water dispersed flows. *Chemical Engineering Science* 2000;55:3133–43.
- [13] Churchill SW. Friction-factor equation spans all fluid-flow regimes. *Chemical Engineering* 1977;84:91–2.
- [14] Kress TS, Keyes JJ. Liquid phase controlled mass transfer to bubbles in cocurrent turbulent pipeline flow. *Chemical Engineering Science* 1973;28:1809–23.