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Experimental verification of CO₂ dissolution rate Due to diffusion induced convection

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Abstract

An experimental setup has been designed for measuring the dissolution rate of buoyant CO₂ into the water phase below. Experiments were performed in a high-pressure cell, where the water phase was stabilized by a porous medium to mimic the situation of a gas cap in a storage reservoir. As many previous tests have been performed in 2D cells, this setup allows for 3D measurements of diffusion-induced convection. The tests are performed at high pressure where CO₂ is at high density, similar to a real storage situation and the dissolved CO₂ is measured by metering the pump that is automatically maintaining constant pressure. This allows rate measurements in a 3D environment. The basic interest was to determine the dissolution rate in the convective regime, but also the diffusion coefficient of CO₂ in water was determined by this experimental setup. In addition, the onset time of convection was estimated. The result show that the dissolution rate measured during convection was one to two order of magnitude faster than predicted by semi-empirical correlations obtained by numerical simulations. The estimated onset time of convection was shorter than theoretical prediction. The overall results suggest that diffusion induced convection plays a more important role than previously assumed.

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1. Introduction

Dissolution of CO₂ in water has received considerable interest in CO₂ storage topic. Several authors have addressed the importance of diffusion-induced convection in CO₂ storage in aquifer. Lindeberg and Wessel-Berg [1] pioneered this concept and pointed out the importance of natural convection for CO₂ sequestration in aquifers. The CO₂ solution is denser than the pure liquid (*e.g.* water) and the liquid column will be metastable or unstable in the gravity field. Convection will increase CO₂ solubility in water and can be important in long-term behaviour of CO₂ storage projects. The instability of diffusive boundary layer, or diffusion-induced convection, has been studied in some papers in recent years. However, very few experimental data, containing mass transfer between water and CO₂ under conditions of natural convection have been published.

There has been a lot of focus on the critical wavelength and onset time of convection of this dissolution mechanism while there has been less focus on the dissolution rates after convection has started. An obvious reason is that the rate cannot readily be derived mathematically due to the nonlinearity of the problem and therefore most studies are performed by numerical simulations. Empirical equations for CO₂ flux has been suggested, by Lindeberg and Wessel Berg [2] for an infinitely high liquid column and Neufeld *et al.* [3] for a liquid column with height, h respectively:

$$J = 1.5 \cdot 10^6 \frac{D}{\tau} (\Delta c_0 \varphi)^2 \left(\frac{\Delta \rho g k}{\mu} \right) \quad (1)$$

$$J = 1.9 \omega_{CO_2} \left(\frac{\Delta \rho g k}{\mu} \right)^{0.8} \left(\frac{\varphi D}{h \tau} \right)^{0.2} \quad (2)$$

Where $\Delta \rho$ is the density difference between CO₂ saturated water and unexposed water, Δc_0 is the CO₂ concentration difference between CO₂ saturated and the initial CO₂ concentration in water, μ is the water viscosity, g is the coefficient of gravity, φ is the porosity, k is the permeability ω_{CO_2} is the mass fraction of CO₂ in water and D is the diffusion coefficient for CO₂ in water. τ is the tortuosity defined as the actual diffusion distance between two points in the porous medium divided on the distance between them ($\tau > 1$). Note that the inverse definition is used in some literature. To test these expressions, an experimental setup has been developed that can perform rate measurements at reservoir condition with CO₂ and water in a porous medium.

Kneafsey and Pruess and Taheri *et al.* [4, 5] used a Hele-Shaw cell to study the CO₂ dissolution rate. Numerical simulation of the experiment showed good agreement with the experiments for onset time of convection and advancement of convective fingers. Weir *et al.* and Farajzadeh *et al.* [6, 7] performed experiments in bulk where a column of CO₂ at high pressure was in contact with water and showed that mass-transfer rates can be measured in a relatively simple pVT cell. Yang and Gu [8] performed experiments in the same system, which was limited to short time behaviour and the long-term behaviour was not measured.

Some studies have been performed using analogue fluid system instead of real CO₂ and brine. Yildiray *et al.* [9] performed experimental study on CO₂ injection into saline aquifer. They used two different porous media, a cylindrical glass tube packed with glass beads of uniform size (0.4 mm in diameter) and a quasi 2D model packed with the same size glass beads using glycerol/water-rich phase represented the injected, wetting phase and heptane-rich phase for non-wetting, displaced phase. Neufeld *et al.* [3] studied convective dissolution of CO₂ in saline aquifer using an analogue fluid system to support their numerical analysis.

Arendt *et al.* [10] studied interaction of interfacial convection and mass transfer effects in CO₂-brine system using a Schelieren method and a three mode magnetic suspension balance connected to an optical cell to analyze the mass transfer of the CO₂-water system up to 360 bar at a temperature of 25 °C. The results were compared with

empirical predictions and good agreement between the model and experiment was obtained. Mathematical modeling and field scale simulation showed that convective mixing can occur in a time range of years to decades when CO₂ is injected into saline aquifer depends on rock and fluid characteristics. Vella and Hupper [11] studied CO₂ injection in Sleipner field in offshore Norway, where around 10⁹ kg of CO₂ is injected to a 200 m thick layer each year and showed that onset time of convection may vary between a few days and 14.2 years. This study clearly shows that the effect of gravity instabilities (convection) could be an important phenomena in the field. Vosper et al. [12] studied the onset of convection in a 2D experiment, but did not make any estimats of the dsissolution rates.

2. Theory

In the governing equation of diffusion (Fick's first law) the diffusion coefficient, D_i , is defined as the proportionality coefficient between the flux of component i , J_i , and the negative concentration gradient of the same component. In one dimension this will be:

$$J_i = -D_i \frac{\partial c_i}{\partial z}, \quad (3)$$

Where c_i is the concentration of component, i and z is the space parameter. By combining Fick's first law with the continuity equation in one dimension:

$$\frac{dC}{dt} = -\frac{dJ}{dz}, \quad (4)$$

The so-called Fick's second law is obtained. In a binary system, there is only one independent concentration parameter, so the equation can be written:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2}, \quad (5)$$

In equation 3, c is the concentration of the gas molecules in the liquid. In the experimental setup that is suggested here, the concentration is maintained constant, c_0 , at one end of the diffusion zone and the length of the liquid column is much longer than the affected zone. With a semi-infinite boundary condition in a porous medium with porosity ϕ and tortuosity, τ ($c = c_0, z = 0$ for all t and $c = 0, z > 0$ for $t = 0$) equation 5 has the solution

$$c = c_0 \left(1 - \operatorname{erf} \left(\frac{z}{\sqrt{(2D\phi t) / \tau}} \right) \right), \quad (6)$$

If the experiment lasts for a long time the finite length, L , of the cell may violate the semi-infinite boundary condition for large t and in this case, the solution of equation 5 will be:

$$c = c_0 \left(1 - 2 \sum_{n=0}^{\infty} \frac{e^{-\pi^2 (n+0.5)^2 D\phi t / \tau L^2}}{\pi (n+0.5)} \sin \left[\pi (n+0.5) \frac{z}{L} \right] \right), \quad (7)$$

In the simplest version of the experiment, the cell has constant volume. When gas is injected, liquid is withdrawn from the bottom of the cell. The cell is closed in both ends at pressure p_0 , and the pressure drop and temperature are

recorded as a function of time. The pressure, p , in the cell will decline according to following equation derived from equation 6:

$$p = p_0 - \frac{2Ac_0ZRT}{V_g} \sqrt{\frac{D\varphi}{\pi\tau}}(t+t_0), \quad (8)$$

Where A is the contact area between gas and liquid, c_0 is the surface concentration of CO_2 , Z is the compressibility factor for CO_2 , R is the gas constant, T is absolute temperature and V_g is the initial gas volume of CO_2 .

$\tau = 1.41$ is often used for randomly packed mono-disperse spheres. When the pressure decreases, the CO_2 solubility in water will decrease and the boundary condition is no longer constant ($c = c_0$). If the pressure decreases too much, free gas bubbles may then be created in the porous medium, changing the transport conditions radically condition in the experiment. An alternative method used here, is to keep the pressure constant and accurately meter in the exact amount of CO_2 that is needed to maintain constant pressure. The expression for consumed CO_2 is:

$$V = V_0 - \frac{2Ac_0}{\rho_{\text{CO}_2}} \sqrt{\frac{D\varphi}{\pi\tau}}(t+t_0), \quad (9)$$

Where V_0 is the start volume and ρ_{CO_2} is the density of CO_2 . The density is calculated as function of pressure and temperature with an equation of state [13]. For a cell with finite length, L , the corresponding equation is:

$$V = V_0 - \frac{2Ac_0}{\rho_{\text{CO}_2}} \sum_{n=0}^{\infty} \frac{e^{-\pi^2(n+0.5)^2 \frac{D\varphi(t+t_0)}{\tau L^2}} - 1}{\pi^2(n+0.5)^2}. \quad (10)$$

The diffusion constant is determined by matching the function to the experimental time and volume data by adjusting D .

The Rayleigh number, Ra , is a dimensionless number used to describe the driving parameters for instability and convective mixing of a denser fluid on top of the other fluid in porous media, which is defined as the ratio between gravity and diffusive forces. In a porous medium, this is defined as:

$$Ra = \frac{\Delta\rho g k H \tau}{\varphi D \mu}. \quad (11)$$

Where H is the porous bed thickness. From stability analysis, the onset time for convection has been determined to

$$t_{crit} = 48.7 \frac{D}{\tau} \left(\frac{\varphi \mu}{k \Delta \rho g} \right)^2. \quad (12)$$

3. Experimental setup and procedure

A schematic of the experimental setup, which was designed for diffusion-convection experiment at high-pressure high-temperature, is given in Figure 1. A high-pressure vessel with liquid temperature control was filled with a porous medium of 90 μm glass beads almost to the top and with the liquid under study. Temperature was measured with platinum resistance elements in top, bottom and in the gas cap with variation within ± 0.005 $^\circ\text{C}$. Both pump and high-pressure vessel were insulated to reduce influences from ambient temperature change. A pressure noise of

± 0.01 bar was found to be due to a digital noise in the pressure device itself. The magnitude of the noise is not critical itself for the measurements since the processing of the data can correct for some of the noise. However, the pressure signal is used to control the pump and this has given some spurious feedback, which has increased the noise. The Helium porosity of the glass bead pack was determined by measuring the void in the packed cell while it was still dry. The porosity was measured to 0.23 by a Helium porosity measurement method and the permeability was measured by water flooding to $4 \cdot 10^{-12} \text{ m}^2$.

The cell was then evacuated and saturated with distilled water. The water permeability of the glass bead pack was measured by flooding with distilled water. To avoid formation of free gas in the sand beads it was important to use de-gassed water to obtain stable measurements. The cell was pressurised to 65 bars with water only. At constant pressure, CO_2 was then injected from the top of the cell to displace sufficient water through the bottom valve to allow the CO_2 to reach a level > 1 mm above the glass bead pack. When the correct amount of water has been displaced, the valve in the bottom of the cell was closed. This point in time represents the start of the experiment. It is assumed that at the interface between liquid and gas the liquid will be saturated with gas and keeps the saturation concentration throughout the experiment. A modified stepper motor controlled Ruska pump filled with CO_2 was temperature controlled by the same liquid thermostat as the cell. A Paros Scientific pressure transducer on the pump was interfaced to a computer, which controlled the pump to maintain pressure, in this case, 65.0 bar. Pressure, pump position (volume), temperature in pump and in the top and bottom of the cell was logged at frequent intervals. Pressure and temperature were kept constant as 65 bar and $20 \text{ }^\circ\text{C}$ within $\pm 0.005 \text{ }^\circ\text{C}$ and pressure noise of ± 0.01 bar.

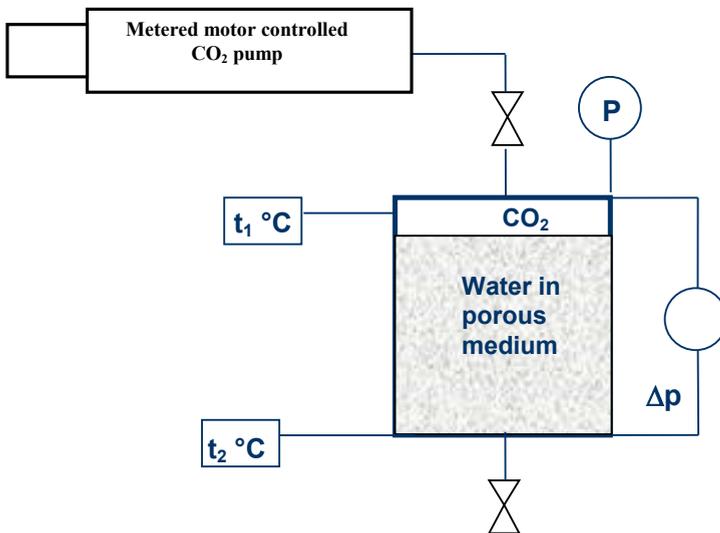


Figure 1. Schematic of apparatus.

4. Experimental results and discussions

Details from some of the tests are illustrated below. Raw data from the log is plotted in Figure 2 to illustrate the level of noise in the measurements. The graph shows three curves, pressure, volume and temperature. The variation in temperature is typically within $\pm 0.02 \text{ }^\circ\text{C}$ and the variation in pressure within ± 0.001 bar, which is quite acceptable. The recorded volume replacement data from the CO_2 pump is corrected for pressure and temperature

variation effects. The result of one of the test is illustrated in Figure 3 for the first ten hours. To identify the diffusion regime, it is however, necessary to plot the curve on the different time scale. Magnification of the same test for the first hours is illustrated in Figure 4.

The diffusion equation was fitted to the data by minimizing the root mean square differences giving an effective diffusion coefficient of $0.815 \cdot 10^{-9} \text{ m}^2/\text{s}$, taking the porosity into account (0.23) and assuming a tortuosity of the square root of 2, this will give a bulk diffusion coefficient of $5.01 \cdot 10^{-9} \text{ m}^2/\text{s}$. This appears to be too high indicating that the setup was not optimal for measuring the diffusion coefficient. The tortuosity equal to the square root of 2 is corresponding to the theoretical value for a monodisperse sphere packing. To give an accurate tortuosity it needs to be measured experimentally.

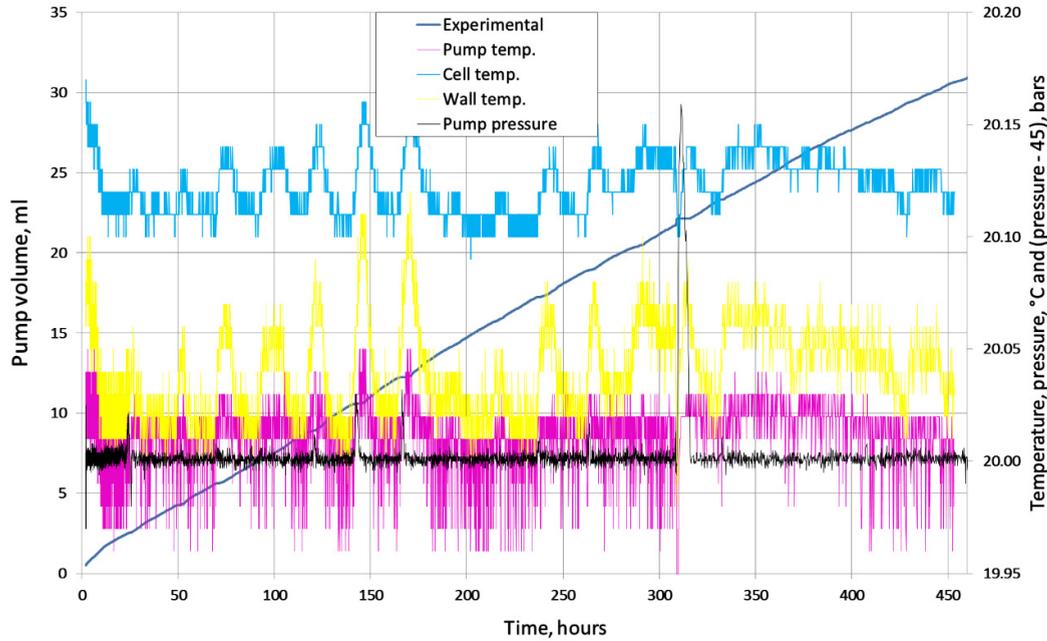


Figure 2. Volume added, temperature, and pressure as function of time for 460 hours in one of the test illustrating the noise levels in the measurements.

The experimental results are given in Table 1 and the experimental conditions and calculated data are summarised in Table 2. The experimental and calculated values are compared in Table 3.

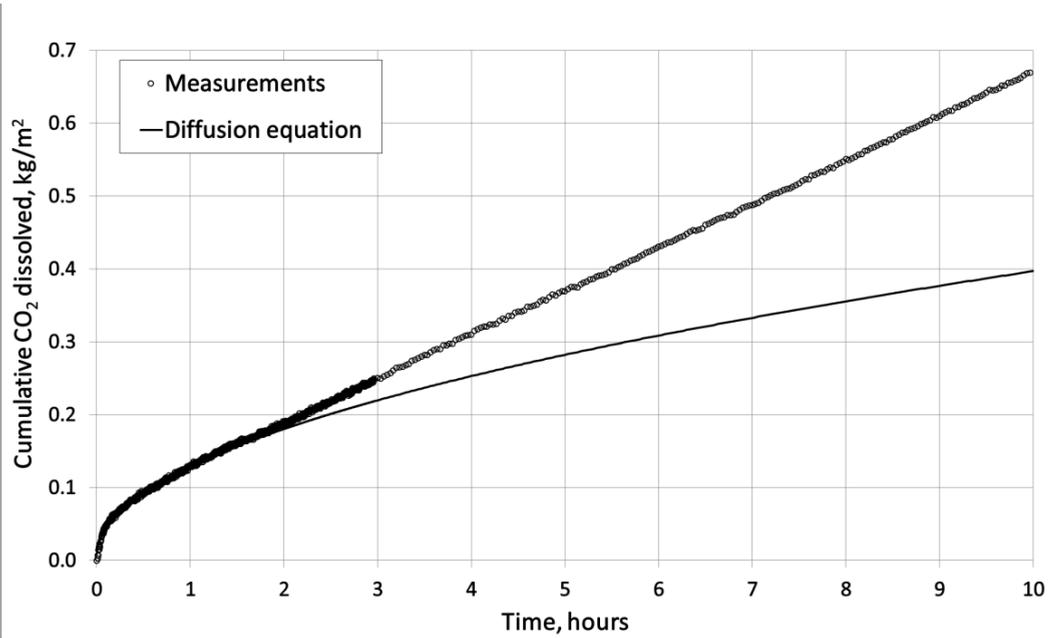


Figure 3. The first 10 hours of corrected measurements compared to a pure diffusion curve. The onset of convection occurs approximately after 2 hour in this test.

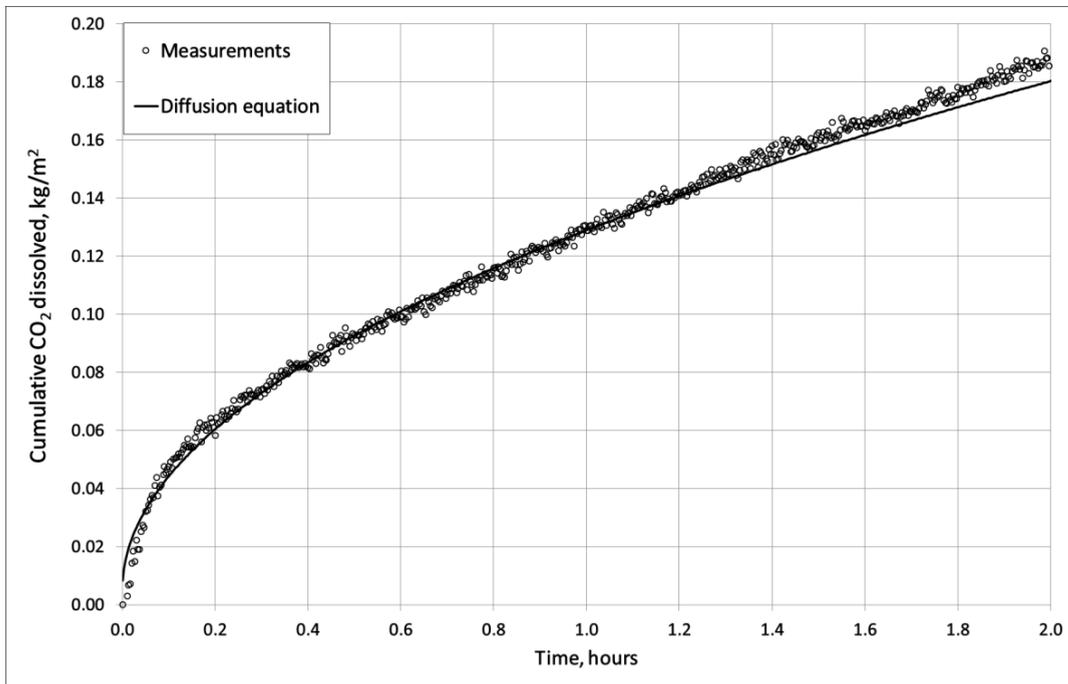


Figure 4. The first 2 hours of corrected measurements compared to a pure diffusion curve.

Table 1. Experimental fluxes

| Test | Flux, kg/(m ² s) |
|-------------|--------------------------------|
| 1 | 1.3 · 10 ⁻⁶ |
| 2 | 2.8 · 10 ⁻⁶ |
| 3 | 1.9 · 10 ⁻⁶ |
| Average | 2.0 · 10 ⁻⁶ |
| Stand. dev. | 0.75 · 10 ⁻⁶ |

Table2. Experimental and calculated data

| Parameter | Symbol | Unit | Value |
|--|-----------------------------|-------------------|-------------------------|
| Pressure | p | bar | 65 |
| Temperature | t | °C | 20 |
| Porosity | φ | | 0.23 |
| Water viscosity | μ | Pa s | 0.001001 |
| Max density change | Δρ | kg/m ³ | 12.63 |
| Acceleration of gravity | g | m/s ² | 9.8065 |
| Solubility of CO ₂ | c ₀ | kg/m ³ | 65.36 |
| Solubility of CO ₂ , mass fraction | ω _{CO₂} | | 0.0639 |
| Contact area of glass bead pack | A | m ² | 0.01116 |
| Height of glass bead pack | H | m | 0.11 |
| Permeability | k | m ² | 4.0 · 10 ⁻¹² |
| Tortuosity = 2 ^{0.5} | τ | 1.41 | 1.41 |
| CO ₂ diffusion coefficient, bulk | D | m ² /s | 2.56 · 10 ⁻⁹ |
| CO ₂ effective diffusion coefficient, D/τ | D _{eff} | m ² /s | 1.81 · 10 ⁻⁹ |
| Rayleigh number | Ra | | 38.3 |

Table 3. Experimental and calculated data compared.

| Parameter | Symbol | Unit | Experimental | Calculated |
|--|-------------------|-----------------------|------------------------|------------------------|
| Onset time of convection comp to Eq. 12 | t _{crit} | hours | 2.0 | 3.26 |
| Dissolution flux after onset comp with Eq. 1 | J | kg/(m ² s) | 1.3 · 10 ⁻⁶ | 3.7 · 10 ⁻⁷ |
| Dissolution flux after onset comp with Eq. 2 | J | kg/(m ² s) | 1.3 · 10 ⁻⁶ | 2.8 · 10 ⁻⁸ |

5. Conclusion

The results show that when dissolution process has entered the convective phase, the dissolution is nearly linear and the experimental dissolution rate is significantly faster than the values calculated with Equation 1 and 2. The experimental value is 5.8 times faster than the value calculated with Equation 1 and 78 times faster than the value calculated with Equation 2 as illustrated in Table 3. In addition, the experimental onset time is shorter than calculated by Equation 12. The overall results suggest that diffusion induced convection plays a more important role than previously assumed.

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