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Effect of Salinity and Pressure on the Rate of Mass Transfer in Aquifer Storage of CO₂

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SUMMARY

The growing concern about global warming has increased interest in improving the technology for the geological storage of CO₂ in aquifers. One important aspect for aquifer storage is the rate of transfer between the overlying gas layer and the aquifer below. It is generally accepted that density driven natural convection is an important mechanism that enhances the mass Transfer rate. There is a lack of experimental work that study the transfer rate into water saturated porous medium at in-situ conditions, i.e., above critical temperatures and at pressures above 60 bar. Representative natural convection experiments require relatively large volumes (e.g., a diameter 8.5 cm and a length of 23 cm). We studied the transfer rate experimentally for both fresh water and brine (2.5, 5 and 10 w/w %). The experiment uses a high pressure ISCO pump to keep the pressure constant. A log-log plot reveals that the mass transfer rate is proportional to $t^{0.8}$, and thus much faster than the predicted by Fick's law. Moreover, the experiments show that natural convection currents are weakest in highly concentrated brine and strongest in pure water.

Introduction

The International Energy Agency (IEA) proposes large-scale investments in carbon capture and storage (CCS) to mitigate the impact of carbon dioxide (CO₂) emissions from the power and industrial sectors. In fact, IEA explicitly claims that two-thirds of today's proven reserves of fossil fuels still need to be in the ground in 2050 if the world is to achieve the 2°C goal, unless carbon capture and storage (CCS) technology can be widely deployed (International Energy Agency, 2012; Khosrokhavar *et al.*, 2014b). Carbon sequestration options include storage in oil and gas reservoirs, saline formations, un-mineable coal seams, basalts, and shales. Perhaps the most commonly considered target repository for CO₂ is a deep saline aquifer. However, concerns for storage in saline formations contain energy requirement (Iijima *et al.*, 2011), cost, long-term storage, impact on seismicity, and the logistics of sequestration (Tao and Clarens, 2013) prevent large scale implementation. Eftekhari *et al.* (2012) investigated the practical exergy requirement in CO₂ capture processes. They showed that exergy consumption for capture varies between 0.5-10 MJ/kg CO₂, corresponding to 2.5% - 50% of the exergy of methane. It illustrates the importance of the methods chosen and the effect of energy consumed to carry out carbon capture and storage. Michael *et al.* (2010) reviewed the experience from existing storage operations for geological storage of CO₂ in saline aquifers. Experience with CO₂ injection at the pilot projects (Frio, Ketzin, Nagaoka and US Regional Partnerships) and existing operations (Sleipner, Snøhvit and In Salah) show that CO₂ geological storage in saline aquifers is technically feasible. By the end of 2008, approximately 20 Mt of CO₂ had been successfully injected into saline aquifers by existing operations. The highest injection rate and total storage volume for a single storage operation are approximately 1 Mt CO₂/year and 25 Mt, respectively. A benchmark study on problems related to CO₂ storage in geologic formations were carried out by Class *et al.* (2009). They mention several problems such as: leakage through a well, spillage of methane into the atmosphere, and low injectivity and heterogeneity of the reservoirs. Quantitative estimation of CO₂ leakage from geological storage was also studied by Celia *et al.* (2004). Their analytical solutions suggest a promising avenue for leakage analysis at the large scale.

It can be expected that optimal storage (Eftekhari *et al.*, 2012) of CO₂ in aquifers improves by dissolution of CO₂ in formation brine because the virtual density (inverse partial molar volume) of dissolved CO₂ in water (1333 kg/m³) is more favorable than its density in the supercritical gas-phase. The sequestration capacity of CO₂ in aquifers would be of the order of 2% of the reservoir volume, if CO₂ would not dissolve in the aqueous phase (Van der Meer, 1992). Injected CO₂ moves upward to the top of the reservoir forming a gas layer due to buoyancy forces. The CO₂ transfer rate from the gas layer to the aquifer below would be slow if it were only determined by molecular diffusion. CO₂ mixes with the water (or brine) to form a denser aqueous phase (e.g., in a pure CO₂-water mixture, the density increase $\Delta\rho \sim 8 \text{ kg/m}^3$ at 30 bar, see, (Gmelin, 1973)). A denser phase above a less dense phase initiates convective currents that enhance the dissolution rate, thus accelerating dissolution of CO₂ in the aqueous phase. The initial stage of natural convection in a saturated porous layer with a denser fluid on top of a lighter fluid has been extensively studied by means of a linear stability analysis, numerical simulations and the energy method ((Bachu *et al.*, 1994; Class *et al.*, 2009; Dentz and Tartakovsky, 2009; Elder, 1968; Ennis-King *et al.*, 2005; Foster, 1965; Gasda, 2010; Khosrokhavar *et al.*, 2014c; Meulenbroek *et al.*, 2013; Moortgat *et al.*, 2009; Myint and Firoozabadi, 2013; Nordbotten and Celia, 2011; Nordbotten *et al.*, 2005; Pruess *et al.*, 2003; Ranganathan *et al.*, 2012; Riaz *et al.*, 2006; Van Duijn *et al.*, 2004; Walker and Homsy, 1978)).

Experimental work can be categorized in two fields: visualization of fingers and quantification of the dissolution rate. Visualization experiments are designed to show the unstable flow when water saturated with CO₂ overlays a column of CO₂ free water (or brine) and to visualize the formation, initiation, and development of fingers. Okhotsimskii and Hozawa (1998) visualized the convective currents in a binary CO₂-water system and qualitatively evaluated the experimental results, based on Marangoni and free (or natural) convection effects in the absence of a porous medium. Kneafsey and Pruess (2010) used a pH indicator to visualize the formation of fingers due to the dissolution of CO₂ in pure water and brine in a Hele-Shaw cell with a permeability around 40,000 Darcy. Khosrokhavar

et al. in a previous paper (Khosrokhavar *et al.*, 2014a) applied the Schlieren method to show the effect of gravity induced fingers in a high pressure cell equipped with windows, in which subcritical or supercritical CO₂ is brought above a liquid water, brine, or oil layer at constant temperature, and compared the results with numerical computations. Neufeld *et al.* (2010) presented a new analogue fluid system that reproduces the convective behavior of a CO₂-enriched brine. Laboratory experiments and high-resolution numerical simulations illustrate that the convective flux scales with the Rayleigh number to the 4/5 power, in contrast with a classical linear relationship. MacMinn *et al.* (2012) studied the spreading and convective dissolution of CO₂ in vertically confined, horizontal aquifers. They conducted the laboratory experiments with analog fluids (water and a mixture of methanol and ethylene glycol) and compared the experimental results with simple theoretical models. Their experiments show that the spreading of the buoyant current is characterized by a parabola-like advance and retreat of its leading edge.

A set of pressure decay experiments were performed by (Farajzadeh *et al.*, 2007; Farajzadeh *et al.*, 2009) to quantify the enhanced mass transfer of CO₂ in water, surfactant solutions, and oil. They showed that the pressure decay results do not match the solution of the Fick's second law. Moghaddam *et al.* (2012) carried out pressure decay experiments in two PVT-cells to investigate the CO₂ dissolution in bulk water and a second set of experiments to study CO₂ dissolution in water saturated porous media with a permeability range of 121 to 2546 Darcy. Based on the experimental results, they calculate a pseudo-dissolution coefficient for CO₂ in water. More recently Moortgat *et al.* (2013) numerically investigated CO₂ injection in vertical and horizontal cores. They showed that an analysis of CO₂ core flooding may provide important parameters for field-scale problems. Benson *et al.* (2013) mention the main criteria for successful large-scale geologic CO₂ storage. They showed that optimizing the design and operation of injection projects will depend on knowledge of the injectivity, trapping capacity, the distribution of CO₂ in the subsurface and the overall areal extent of the subsurface plume.

The objective of this paper is to design and construct an experimental set-up, with which the effect of salinity and pressure on the rate of mass transfer in aquifer storage of CO₂ can be elucidated.

The structure of the paper is as follows: first we describe our experimental set-up and briefly explain the procedure. Then we investigate the onset and development of natural convection and quantify the mass transfer rate in our experimental configuration and interpret the results. Finally we end the paper with some concluding remarks.

Experimental Set-up

The experimental set up, shown in Figure 1, consists of a stainless steel vessel with an inside diameter of 8.43 cm and a height of 22.7 cm (see Figure 2). It is positioned vertically in an oven with a temperature control accuracy of 0.02 K. The top opening of the vessel is connected to a pressure transducer with an accuracy of 0.01 bar. The pressure is recorded by data acquisition software every 5 seconds.

The experimental procedure is as follows: First, the vessel is filled with known mass of sand with a known particle size distribution. 90% of the Cylinder is filled with sand pack to ensure that the sand particles are completely packed, the vessel is shaken by hammering the wall for 60 minutes. The vessel is mounted in the oven and filled with helium at 8 bar. We use the helium detector to check the connections for the leakage. Afterward we pressurized the cylinder by helium to 100 bar. Then we record the helium pressure for 24 hours. If there is no noticeable pressure decline (no leakage) we flush the sand pack with CO₂, 4-6 times. Then, we connect the set up to a vacuum pump for 24 hours. The vacuuming step is necessary to prevent the formation of bubbles of gas in the water saturated zone. Then a known mass of water is injected through valve 5 to saturate the sand pack. The vacuum in the vessel is enough to suck water inside. Then we bring CO₂ into the ISCO PUMP at 60 and 100 bar. Both the ISCO pump and cylinder containing the sand pack are in the oven to keep the

temperature constant. We leave the set-up in the oven for 24 hours to reach thermal equilibrium at a constant temperature of 35°C. When the system reached thermal equilibrium, we start the data acquisition system and inject CO₂ at constant pressure into the vessel through valve 3.

Figure 1 Schematic drawing of the experimental set-up. Mention purpose of all valves.

Figure 2 Cylindrical high pressure cell. ($A=88.9\text{ mm}$, $B\text{ (Height)}=227\text{ mm}$ and $T=4.6\text{ mm}$).

The position of the ISCO PUMP piston, which is adjusted to keep the pressure constant, is measured as a function of time. From this the consumed volume history is determined and recorded every 5 seconds for about 40 hours.

Experimental results and discussion

We carried out five experiments all at a constant temperature and pressure. Figure 3 shows the five experimental results after 40 hours at temperatures, pressures and salinities $(T, P, c) = (308 \text{ K}, 100 \text{ bar}, 10 \text{ w/w\%})$, $(308 \text{ K}, 100 \text{ bar}, 5 \text{ w/w\%})$, $(308 \text{ K}, 100 \text{ bar}, 2.5 \text{ w/w\%})$, $(308 \text{ K}, 100 \text{ bar}, 0 \text{ w/w\%})$ and $(308 \text{ K}, 60 \text{ bar}, 0 \text{ w/w\%})$. It illustrates that increasing salinity decreases the consumed CO_2 .

Figure 3-a to Figure 3-e show the consumed volume versus time for the five experiments, respectively. To show the importance of enhanced dissolution of CO_2 , the results are compared to the pure diffusion model. Initially, the consumed volume is zero. By dissolving CO_2 in water (or the NaCl solution), the number of moles of CO_2 in the sand pack increases and consequently the volume measured in the ISCO pump decreases. The consumed volume is controlled by the rate of mass transfer of CO_2 into water (NaCl solution), which is diffusion controlled at the start of the process. However, experimental curve deviates from the pure diffusion curve predicted by a diffusion model and has a slope bigger than $\sqrt{t}$. As the slope is larger than 0.5 it shows that in all cases we have enhanced diffusion. The deviation from pure diffusion, if it occurs, starts before 30 seconds and would be smaller than known onset times in porous media (see Table 2).

Figure 3a presents the result for a 10 w/w% NaCl solution at 100 bar and 35°C . At this salt concentration there is a smaller density difference between the CO_2 solution and the pure brine solution (Duan and Sun, 2003) and consequently the Rayleigh number is relatively low. The experiment starts after admitting CO_2 into the cell at the required pressure. At 5000 seconds, 2.50 cm^3 of CO_2 was consumed. After that the slope of experimental curve has changed. From 5000 to 140000 seconds, another 7.50 cm^3 of CO_2 dissolved. In comparison to the theoretical diffusion model, the number of moles dissolved in the high pressure cell, i.e., the experimental set-up is about five times bigger. In the early stages of the experiment the consumption rate of CO_2 is faster than in the later stages.

Figure 3b shows the experimental curve for a 5 w/w% NaCl solution at 100 bar and 35°C . Following Eq. (1) we expect that more CO_2 is dissolved than for the 10w/w% solution. Table 2 shows that the Rayleigh number decreases for increasing salt concentrations. Also the Henry's constant is smaller for decreasing salinity. The solubility of CO_2 in 5 w/w% NaCl solution is less than in pure water, but larger than in the 10 w/w% case, leading to smaller and larger Δp values respectively. From $t=0$ to $t=5000$ seconds 2.75 cm^3 of CO_2 has been dissolved. As time proceeds, the slope of the curve is increasing. Between $t=5000$ and $t=55000$ about another 6.35 cm^3 of CO_2 dissolved and after that the slope has changed again.

Figure 3c shows the result for the system of a 2.5 w/w% NaCl solution at 100 bar and 35°C . We observe that the deviation from diffusion model appears in early stages; however, as time elapses the slope of the curve increases. Figure 3c shows that at $t=5000$ seconds, the consumed volume was about 3.15 cm^3 . From $t=5000$ to $t=100000$ seconds the volume dissolved has increased to 12.80 cc and after that till the end of experiment it fluctuates to reach its end value.

Figure 3d demonstrates the experimental result for the CO_2 – water system at 100 bar and 35°C . From $t=0$ to $t=6000$ seconds the experiment run with lower slope in comparison to late stages. A more or less similar behavior is observed for subcritical critical CO_2 - water system (Figure 3e).

Figure 3e illustrates the experimental pattern for the CO_2 -water system at 60 bar and 35°C . After bringing CO_2 to the cell, the system exhibits similar behavior in comparison to other experimental results however the instability occurred later. After 5000 seconds around 14 cm^3 of CO_2 dissolved. From $t=3000$ to $t=140000$ seconds the slope of experiment has smoothly changed. In comparison with supercritical experiments, at 60 bar the consumed volume is larger. To investigate late time behavior in our experimental approach, we have plotted volumetric consumption rate in experimental set-up versus time. The results are shown in Figure 4. One observes more or less same behavior for all experiments in late stages. At 100 bar, in all cases the fast decrease in rate can be seen, after hitting

the bottom of the cell, it starts to increase and fluctuate to reach a plateau. At 60 bar the same process occurred in later times. In our experimental results, the surface tension increases (Li *et al.*, 2012). It could be a possible reason to have both mechanisms (natural convection and Marangoni effect) in our study (Arendt *et al.*, 2004). We leave more investigation for future work.

Figure 3 Experimental results at 100 bar and 308K. It demonstrates four experiments at different salinity from 0 wt% to 10 wt%. By increasing the salinity, the amount of CO₂ dissolved in the brine decreased. Experimental result at 60 bar and 308K, it shows at constant pressure, about 72 cc CO₂ was consumed.

Figure 4 The volumetric consumption rate is plotted versus time.

Data Analysis

We carried out five experiments all at a constant temperature and pressure. To illustrate the importance of the enhanced dissolution of CO₂, the results are compared to results computed with a diffusion model.

By dissolution, CO₂ starts to diffuse into the sand pack, which is saturated with water (or NaCl solution) the part of the moles of CO₂ is transferred from the ISCO pump to the sand pack. The amount of CO₂ dissolved in the aqueous phase in the sand pack is controlled by the rate of mass transfer of CO₂. The mass transfer is initially diffusion controlled. However, after some time the experimental curve deviates from the diffusion model. An accurate experimental measurement of the flux for the actual CO₂-brine system is difficult. For porous media, a large number of numerical studies (Ennis-King *et al.*, 2005; Riaz *et al.*, 2006) show that the onset time of convection is inversely proportional to the Rayleigh number, which can be expressed as,

$$t_0 = c_0 Ra^{-1} = c_0 \left(\frac{\phi \mu \sqrt{D}}{kg \Delta \rho} \right)^2 \quad (1)$$

where μ [Pa.s] is the viscosity of the aqueous phase, ϕ [-] is the porosity of the porous medium, D [m²/s] is the binary diffusion coefficient of CO₂ in the brine saturated porous medium, g [9.81 m/s²] is the acceleration due to gravity, k [m²] is the permeability of the porous medium, and $\Delta \rho$ [kg/m³] is the difference between the density of pure solvent and the solvent saturated with the solute. Moreover, c_0 is a constant value and it covers a range between 55 and 4500. Many investigations are applied to quantify the onset time. Our experimental work is summarized in Table 1.

Table 1 The summary of experimental work.

	p [bar]	T [C°]	Salinity	k	ϕ	μ (Bando <i>et al.</i> , 2004)	$\Delta\rho$ (Duan and Sun, 2003)	D (Sell <i>et al.</i> , 2012)	K_H [Pa.m ³ /mol]	Ra
Experiment 1	100	35	10W/W%	59×10^{-12}	0.40	9.34×10^{-4}	7.32	1.30×10^{-9}	12500	1390
Experiment 2	100	35	5W/W%	59×10^{-12}	0.40	8.56×10^{-4}	9.86	1.50×10^{-9}	10500	1777
Experiment 3	100	35	2.5W/W%	59×10^{-12}	0.40	8.25×10^{-4}	11.32	1.75×10^{-9}	9000	1794
Experiment 4	100	35	0.0W/W%	59×10^{-12}	0.40	8.00×10^{-4}	12.91	2×10^{-9}	7500	1868
Experiment 5	60	35	0.0W/W%	59×10^{-12}	0.40	7.99×10^{-4}	10.97	2×10^{-9}	6000	1584

The experimental onset times are presented in Table 2 and are compared to the theoretical relations, derived by Riaz *et al.* (2006), Ennis-King *et al.* (2005), Hassanzadeh *et al.* (2007), Xu *et al.* (2006), Pau *et al.* (2010) and Meulenbroek *et al.* (2013).

Table 2 The experimental onset times are compared with different theoretical models.

	Xu <i>et al.</i> (2006)	Ennis-King <i>et al.</i> (2005)	Riaz <i>et al.</i> (2006)	Pau <i>et al.</i> (2010)	Hassanzadeh <i>et al.</i> (2007)	(Meulenbroek <i>et al.</i> , 2013)	Experimental onset time/[sec] (this paper)
Experiment 1	761	789	3695	18126-37152	5061	556	~early stages
Experiment 2	405	420	1966	9646-19772	2693	296	~ early stages
Experiment 3	333	345	1618	7939-19272	2216	243	~ early stages
Experiment 4	275	285	1337	6559-13444	1831	201	~ early stages
Experiment 5	382	396	1855	9101-18654	2541	279	~ early stages

In order to quantify the time evolution of the flux, we describe the late time behavior when the plumes have not yet reached the bottom boundary. This period begins in the neighborhood of the start of nonlinear behavior of mass transfer rate versus time. We follow (Farajzadeh *et al.*, 2013b) to characterize the mass transfer rate of CO₂ dissolved in aqueous phase as a function of the Rayleigh number. Comparison between our result and other scientific work has been summarized in Table 3.

Table 3: Comparison between Current experimental result and other scientific works.

	Backhaus <i>et al.</i> (2011)	Slim <i>et al.</i> (2013)	Neufeld <i>et al.</i> (2010)	Nield and Bejan (2006)	Farajzadeh <i>et al.</i> (2013a)	Hidalgo <i>et al.</i> (2012)	Our experimental result
Experimental And numerical works to find a relation between Rayleigh Number and mass transfer rate.	$Sh \sim Ra^{0.75}$	$Sh \sim Ra$	$Sh \sim Ra^{0.83}$	$Sh \sim Ra$	$dm/dt \sim Ra^{0.832}$	$Sh \sim Ra$	$dm/dt \sim Ra^{0.8283}$

Conclusions

- Dissolution of CO₂ in an aqueous phase forms a mixture that is denser than the CO₂ free water or brine. This causes a local density increase, which induces natural convection currents (gravity fingers) when gaseous CO₂ is brought above the liquid phase. This enhances the rate of mixing of CO₂ in the liquid phase.
- We designed and built a cylindrical high pressure cell in which gravity induced fingers (playing a major role in the enhanced mixing process) could have occurred, e.g., by mounting the cylinder horizontally and filling the 90% with sand pack ($k=59$ Darcy and porosity =40%) and then saturating with water or brine and the top with gaseous or sub-supercritical CO₂ at constant pressure.
- The experiments show that natural convection currents are weakest in highly concentrated brine and strongest in pure water.
- The experiments show that CO₂ consumption is bigger in subcritical than supercritical condition.

- The experimental results propose a semi linear relation between mass transfer rate and Rayleigh number.
- To our knowledge, this is the first time that such of experiments are carried out at constant pressure injection in the lab scale with considering the effect of salinities.

Nomenclature

C = concentration (mol/m³)
 C_g = concentration (mol/m³)
 D = molecular diffusion coefficient, (m²/s)
 D_g = molecular diffusion coefficient in gas phase, (m²/s)
 k = permeability, mD
 u = velocity (m/s)
 P = pressure (bar)
 t = time
 ρ = density (kg/m³)
 μ = viscosity of the solvent (kg.m.s)
 g = acceleration due to gravity (kg/m²)
 Ra = Rayleigh number

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