

Visualization of CO₂ absorption in Newtonian and non-Newtonian fluids

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ABSTRACT

In this work we describe experiments done in a simple PVT cell at the University of Stavanger. Pressurized CO₂ is placed as a gas cap over the fluid. CO₂ dissolves and mixes into the water. Traditional theory describes the mixing process as a diffusion process. However, the experiments show that CO₂ absorbs at the interface and (carbonic acid) fingers into the water as a result of Rayleigh-Taylor instability, thus convection seems to be the dominant process. This was first conjectured indirectly from pressure measurements, but the direct proof of the convection was seen by using a novel technique based on adding pH-titration indicators into the fluid. As CO₂ absorbs into the fluid, the pH changes locally and the colour visualizes the CO₂ flow path. The use of pH indicator has a potential of even measuring local concentration of CO₂. The fluids used are water and PAC (polyanionic cellulose) in order to compare the Newtonian versus non-Newtonian behaviour. It turns out that the convection modes are quite different in the two types of rheology. This will be shown in the presentation.

INTRODUCTION

The carbon dioxide-water system is important in many disciplines of science, both physically and industrially. In particular, the dissolution of CO₂ into water is among one of the interesting phenomena

in physical chemistry. Initially, the purpose of this study was generally to investigate the thermophysical properties of CO₂-water mixtures and particularly the condensation processes relevant for oxy-fuel cycles. Large effort was undertaken to find a simple way to understand the mechanism of CO₂ absorption into liquid using an existing PVT cell at the University. This proved to be a large task indeed due to the absence of full visibility of the cell which was considered to greatly would help understand the absorption process.

Visualization is now commonly employed and facilitates the ability to comprehend the process. It has recently been shown that visualization has been used in a Hele-Shaw cell¹ to help capture the physical process in convective diffusion of CO₂ in saline aquifers². pH indicators as well as dyes were used as means of visualization, with the objective to estimate the dissolution rate of CO₂ in aquifers related to enhancing storage security. In addition, these experiments helped to refine or confirm traditional theory and numerical simulators¹.

The mass transfer of CO₂ into a reservoir brine sample was experimentally studied by monitoring the pressure decay inside a closed high-pressure PVT cell³. The cell was made of glass tube and a video-based digital cathetometer allowed direct measurements of phase volumes. It was shown that the mass transfer rate of CO₂ into brine was accelerated due to density-

driven natural convection.

Dissolving CO₂ with water leads to an increase in the mixture density and the gravitational force leads to natural convection. This process in turn increases the concentration at the CO₂ water interface. Thus, the absorption of CO₂ into water is controlled by the mass transfer of gas which can be determined by measurements of pressure decays in the gas phase. By using a PVT cell, Farajzadeh⁴ conducted a study on mass transfer of CO₂ into liquids. It was found that the transfer rate at initial stages of the experiments was faster, and the transfer rate increased with increasing the gas pressure.

REACTION MECHANISM

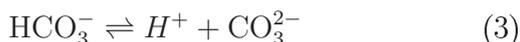
When CO₂ is dissolved into water, carbonic acid is formed. The following chemical equilibrium is established:



Carbonic acid is a weak acid and can dissociate in two steps:



and



Hydrogen ions (H⁺) are released by the generation of bicarbonate and carbonate ions. Therefore, the pH of the solution is lowered and the solubility of CO₂ decreases with decreasing pH. This CO₂ concentration distribution in fluids will be visualized by adding pH-titration indicators into the fluids.

RAYLEIGH TAYLOR INSTABILITY

In the present work we investigate the CO₂ absorption into water as a result of Rayleigh-Taylor instability. Pressure measurements combined with visualization by adding pH-titration indicator helped understand the convection mechanism in Newtonian and non-Newtonian fluids.

When a dense fluid is placed on top of a less dense fluid, an unstable situation arises, known as Rayleigh-Taylor instability⁵. The denser fluid falls into the lighter one, and the lighter fluid displaces upward by convection. Fig. 1 demonstrates the interaction of fluids with different densities⁶.

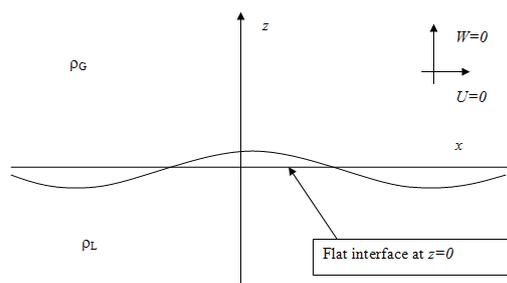


Figure 1: Basic principle of Rayleigh-Taylor instability⁶.

Temperature difference might provide a corresponding small density difference due to thermal expansion. Ramaprabhu and Andrews⁷ conducted experiments in water with a top layer at a temperature of 17°C and the bottom layer at 22°C. This mixing process is illustrated by planar laser induced fluorescence (PLIF) photographs in Fig. 2. It is shown in Fig. 2b



Figure 2: PLIF images of Rayleigh-Taylor instability in two water layers. (a) at early and (b) at late times of evolution⁷.

that an inverted mushroom-shaped structure is formed at late time which are driven by shear as a result of localized Kelvin-Helmholtz instability⁷.

EXPERIMENTAL

A simplified view of the PVT cell is

shown in Fig. 3. It consists of a transparent

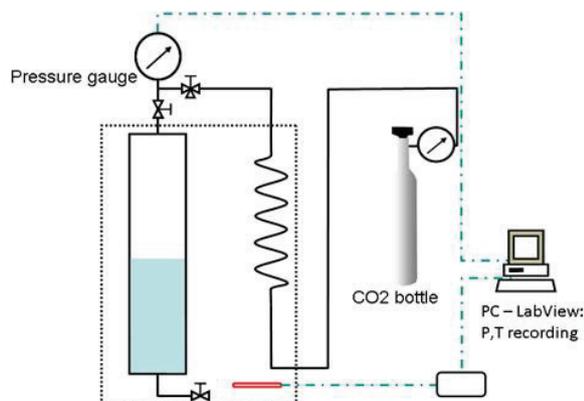


Figure 3: Schematic representation of the PVT cell.

40 cm long acrylic pipe, water bath, a commercial CO₂ bottle from AGA AS, thermoelement, pressure transmitter, a camera and a PC. The water bath is a rectangular box with four sides made of glass. It serves also to both give good optical condition and corrects the refraction of light caused by the pipe curvature. The cell is immersed in the water bath where the temperature is held constant by a Refrigerated / Heating Circulator Model F34-HL from Julabo Laborthechnik GMBH from Germany. The regulation range is -30 to 150°C. In these experiments the water bath was kept at 20°C.

Two valves are connected at the top and the bottom of the cell, respectively. These valves assure that the gas and liquid phase are brought in contact with each other. An absolute pressure transmitter ranging from 0 to 15 bar (Smart Model 3051C, Rosemount) is mounted to measure the inside pressure, via pressure taps on top of the cell. The temperature in the water bath is measured using a Pt 104 sensing element. All instruments were connected via a high speed USB carrier NI-9162 for data acquisition system, using LabView (National Instruments) as programming environment.

Two different concentrations of polyanionic cellulose, PAC regular obtained from

MI-Swaco, were used: 200 and 400 ppm PAC dissolved in water. A Silverson L4R T-A mixer from Laboglass was used for the preparation of the solution before pouring to the tube. The rheological measurements were taken using a Physica UDS 200 rheometer with cone plate configuration MK 24 (75 mm, 1°). The two samples were measured at 20°C with increasing shear rate to the maximum (1020 s⁻¹) and decreasing again to the minimum (1.5 s⁻¹). This was chosen to see any hysteresis effect. It should be noted that the viscosities were measured at ten seconds intervals between the shear rates.

A pH indicator combined with photographic recording appeared to help understanding the absorption processes. Therefore, Brom Thymol blue was added to deionized water to serve as a contrast agent for local determination of CO₂ concentration in water. The pH was measured using a digital pH meter model S20 Seven Easy from Mettler Toledo. The cell was filled with a solution of water and pH indicator via an inlet at the bottom using a procedure to avoid air bubbles being transported with the water. The cell is allowed to fully reach thermal equilibrium inside the water bath. Some time before the injection of the CO₂ gas, some air was first injected from the top to form a thin layer of air. This was done purposely to avoid the Rayleigh-Taylor instability from starting prematurely. Otherwise the CO₂ stream causes a light head of jet from the inlet pipe, which could start a convection via the gas-liquid interface. The CO₂ gas was delivered from a commercial CO₂ bottle (CO₂ purity 99.99%) and was brought to the water temperature by flowing the gas through a metallic coil tube (inner diameter 1/8"). 250 ml of water was then drained to reach a desired liquid height leaving a 7 cm CO₂ gas cap. The bottom valve then closed. The experiments then start by injecting more CO₂ up to a selected overpressure, normally 5-6 bar.

The camera, a Nikon D5000 AF - S DX Nikkor 18-55 mm f/3.5-5.6G VR was set to interval recording using the Camera Control Pro 2 software and a PC.

RESULTS AND DISCUSSIONS

The visualization of CO₂ absorption is carried out for both Newtonian and non-Newtonian water based fluids. The combination of the pressure history plots with visualizations is analyzed. Water was used first. The results obtained from these tests served as a basis and reference for the non-Newtonian fluid.

The viscosity of the fluids used is presented in Fig. 4. It can be seen that the so-

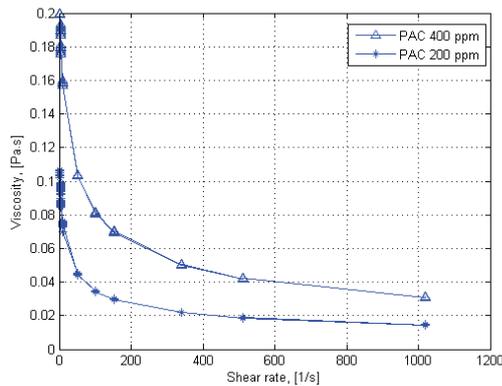


Figure 4: Viscosity versus shear rate at 20°C of the 200 and 400 ppm concentrations of PAC dissolved in water.

lutions are showing shear thinning behavior. The result from pH measurements at ambient temperature before and after each experiment is presented in Table 1.

	Before	After
Water	6.70	4.25
200 ppm	6.80	5.88
400 ppm	6.55	5.38
Color code	blueish	yellowish

The pH results presented from Table 1 show a decrease in pH when the tests were started compared to the end of the process. This is consistent with Eqs. 1 to 3, because as the liquid CO₂ dissolves in water, regions of low pH would form.

Fig. 5 shows a sequential pictures of CO₂ absorption in water. The experiment

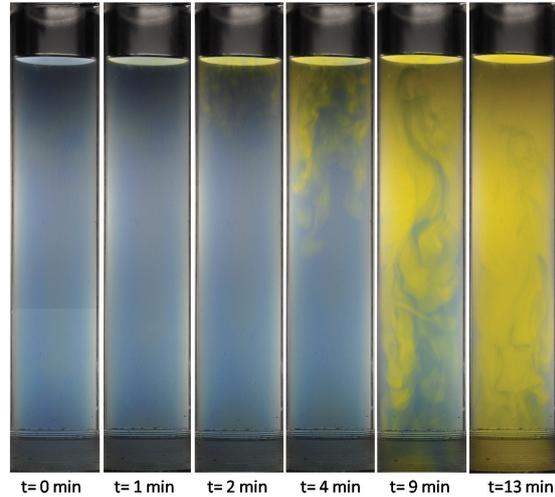


Figure 5: Visualization of CO₂ absorption in water.

starts with CO₂ pressurizing at $t = 0$ and the pH of water is around 7. This can be seen from the color of the fluid in combination with the results of pH measurements presented in Table 1. It is clearly seen from Fig. 5 how CO₂ absorbs at the CO₂-water interface and fingers into the water as a result of the Rayleigh-Taylor instability. After an "induction period" of approximately 1 minute the instability starts when the carbonic acid which is sufficiently denser than water. Carbonic acid moves downward, displacing water upwards. A typical situation can be seen in the image after $t = 9$ minutes. This is consistent with others observation^{1,5,7}. The secondary flow of apparent inverted mushroom-shaped structures are driven partly by shear resulting in local Kelvin-Helmholtz instability⁷, but also via stagnation flow bifurcation patterns. The fingers develop laterally, coalesce and sink downwards¹. At a later stage water that is not laden with CO₂ in the middle of the cell is pushed upward. This convection process also seems to be dominant during the first 20 seconds as shown in Fig. 6. This is consistent with the results

from other authors^{3,4}. In this plot, initially the CO₂ pressure increased because of the compression of CO₂. Once this operation was completed, the CO₂ pressure declined from approximately 5 bar to slightly below 1 bar (overpressure). The solution was uniformly yellowish after approximately 17 min.

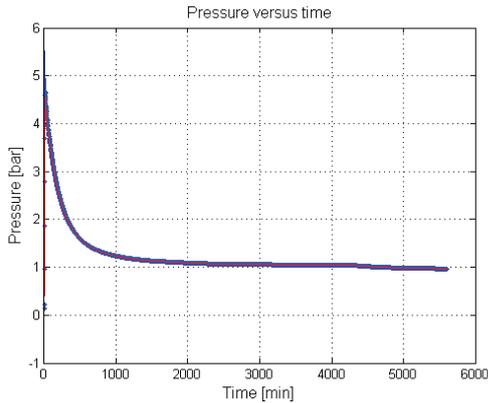


Figure 6: Pressure decline of CO₂ absorption in water starting at 5 bar pressure.

The results from mixing of CO₂ in different concentrations of PAC solutions are quite similar. Therefore, only the trends obtained in PAC400 is presented in this paper. The PAC dissolved in water appeared to be slower compared to water. This is demonstrated in the results shown in Figs. 7 and 8.

It is shown in Fig. 7 that the instability started at 3 min. The CO₂ fingers from both sides first (at $t = 18$ min) and is dragged in to the middle of the cylinder at $t = 33$ min. The viscosity of the fluid seems to attenuate the fingering. As time progressed, the CO₂ laden fluid flows downward but centered ($t = 54$ min). Its width and depth of penetration are increased and pushes water which was not yet laden with CO₂, laterally.

The result from pressure measurement of CO₂ absorption in PAC400 is presented in Fig. 8. The mixture of CO₂ in polymeric fluids lasted longer time compared

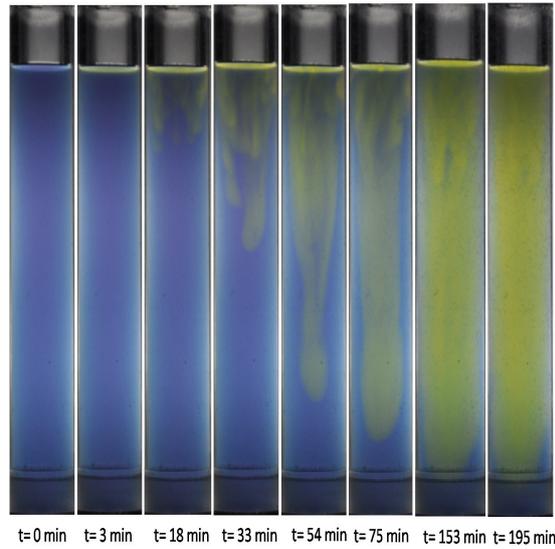


Figure 7: Visualization of CO₂ absorption in PAC400.

to water, not unexpected since the PAC solution has a higher effective viscosity and also shear thinning so that at low velocities the viscosity is apparently even higher at lower convection.

These photographic results were mainly intended to demonstrate the suitability and the potential of the experimental technique. Therefore the discussion of the observed phenomena is restricted.

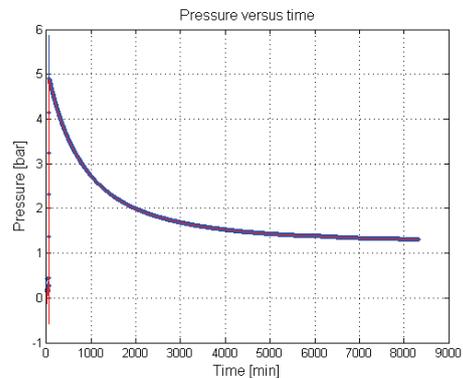


Figure 8: Pressure decline of CO₂ absorption in PAC400 starting at 5 bar pressure.

CONCLUSIONS

This work demonstrates that convection process is the dominant process in CO₂ absorption in Newtonian and non-Newtonian fluid. The PVT cell combined with a novel technique based on adding pH indicators into the fluids provides reliable and valuable interpretation of even measuring local concentration of CO₂. Pressure measurements were not a sufficient tool for identification of the process.

Results from three series of experiments were shown, using water and two different concentrations of PAC. The Rayleigh-Taylor instability may be considered as a mixing process for fluids of different densities.

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