

Numerical and Experimental Investigation of Natural Convection Flow of (Sub-) and (Super-) Critical CO₂ in Aqueous

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Abstract: Optimal storage of carbon dioxide (CO₂) in aquifers requires dissolution in the aqueous phase. The aqueous phase may contain salt, and therefore we will refer to the aqueous phase as brine, even if this study is confined to pure water. In the same way carbon dioxide enhanced oil recovery requires dissolution in the oil phase. Transfer of CO₂ from the gas phase to the aqueous phase or oil phase would be slow if it were only driven by diffusion. Dissolution of CO₂ in brine (oil) forms a mixture that is denser than the original brine. This causes a local density increase, which induces natural convection currents accelerating the rate of CO₂ dissolution.

This study presents numerical models in bulk fluids to simulate a set of high pressure visual experiments based on the Schlieren technique, in which we observe the effect of gravity-induced fingers when sub- and super-critical CO₂ is brought above a liquid at in situ pressures and temperatures.

Keywords: CO₂ Sequestration, Natural convection, Schlieren Method, visualization

1. Introduction

Optimal storage [5] of carbon dioxide (CO₂) in aquifers needs dissolution of CO₂ in formation brine. Without dissolution of CO₂ in the aqueous phase, the storage volume of CO₂ in aquifers would be the order of 2% of the reservoir volume [1]. It can be expected that, due to buoyancy forces, injected CO₂ rises to the top of the reservoir forming a gas layer. Transfer from this gas layer to the aquifer below would be slow if it were only driven by diffusion. However, CO₂ mixes with the water to form a denser aqueous phase (e.g., $\Delta\rho \sim 8 \text{ kg/m}^3$ at 30 bars, see ref. [1]). This induces convective currents and enhances the dissolution rate, which is equivalent to the

dissolution of a larger amount of CO₂ in a shorter period of time. The large volume of dissolved CO₂ remains permanently in the aqueous phase (at least until the pressure remains unchanged) and poses no threat of leakage, which is favorable for geological storage of CO₂. An analogous process occurs for carbon dioxide enhanced oil recovery. This process has been extensively studied also in terms of a linear stability analysis, energy method and numerical simulations [3,4]. The results are usually summarized in terms of the Rayleigh number, which is dependent on the properties of the mixture and the porous medium and is defined as

$$Ra = \frac{k\Delta\rho gH}{\phi\mu D}, \quad (1)$$

where k is the permeability of the porous medium, $\Delta\rho$ is the density difference between the mixture and the brine, g is acceleration due to gravity, H is the characteristic length of the system, ϕ is the porosity, μ is the viscosity of the mixture and D is the molecular diffusion coefficient of CO₂ in water. The onset of the convective currents is inversely related to the square of Ra, i.e., $t_c \propto Ra^{-2}$ [4]. There are many papers devoted to the theoretical description of the convective currents during storage of CO₂ in aquifers. Mass transfer of CO₂ into water has been evaluated experimentally and analytically in different conditions. References [3,4 and 6] studied the occurrence of natural convection, while recording the pressure change in a cylindrical PVT-cell, where a fixed volume of CO₂ gas was brought into contact with a column of distilled water. Based on the experimental results, in the first period of dissolution the mass-transfer rate is much faster than Fick's Law (diffusion-based model) because in addition to molecular diffusion, density-driven natural convection increases the mass-transfer rate. Fig 1

compares the extent of natural convection in the presence and absence of porous medium in a glass tube with a radius of 3.5 mm by tracking the pressure history. In one experiment the glass tube is filled with only water, and in the other one the tube is filled with a porous medium of the same height and saturated with water. This figure shows that, although natural convection enhances the transfer rate in water-saturated porous media, its significance is less compared to bulk liquid.

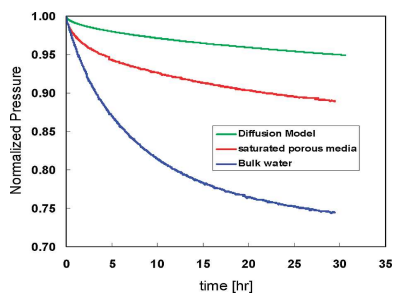


Figure 1: Comparison of the pressure history of the experiments with (red) and without porous media (blue). The experiments were done in a glass tube with radius of 3.5 mm at 11 bar see ref [4].

2. Experimental Set up

A set of experiments have been done to visualize the induced convection currents when carbon dioxide is brought above a layer of liquid water.

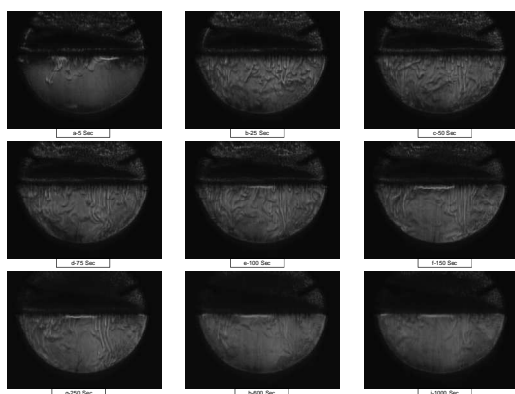


Figure 2: Schlieren pattern in CO₂-Water at different times. It shows fingers in the lower half of the domain. The upper half is filled with CO₂ at 64 bars and T=313 k.[1]

Our method of choice is the Schlieren method, see [1,2]. The results for bulk water are shown in Fig 2. the observed intensities are proportional to the concentration gradient in the Schlieren method.

3. Theory

In this work, we consider a 2-D model for natural convection flow of CO₂ in aqueous phase (see Fig. 3). The diameter of the fluid containing part of the cell is 50 mm and the length is 11.6 mm. The cell is filled with water until the equator. The CO₂ gas is brought on top of the water, after which natural convection starts. We applied the conventional equations for buoyant density flow and the Boussinesq approximation. This approximation uses constant densities except in the gravity term in the Navier Stokes equation. Moreover, we disregard inertia effects. Due to the density heterogeneity the fresh (no-CO₂ containing) water moves to the interface and CO₂ containing water moves downwards, accelerating the mass transfer rate. The boundary conditions are no flow conditions at the vessel boundary. We ignore the boundary conditions for the fluid in contact with the glass windows, assuming that the flow is approximately 2D.

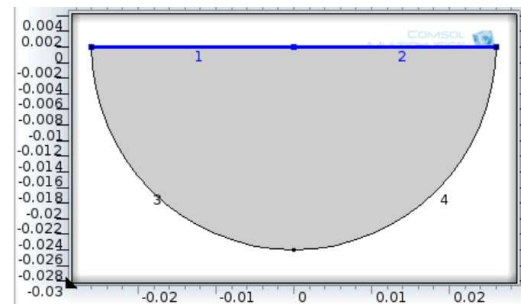


Figure 3: Geometry of the model

4. Governing Equations

3.1 Liquid Phase

(a) Continuity Equation

$$\text{div } \mathbf{v} = 0 \quad (2)$$

(b) Conservation of Momentum, disregarding inertia effects

$$\frac{\partial \mathbf{v}}{\partial t} = -\frac{1}{\rho} \mathbf{grad} \rho + \nu \Delta \mathbf{v} - \beta_c \mathbf{g} \Delta c \quad (3)$$

(c) Concentration Equation.

$$\frac{\partial c}{\partial t} + \mathbf{v} \cdot \mathbf{grad} c = D \Delta c \quad (4)$$

3.2 Gas Phase

$$\frac{\partial c_g}{\partial t} = D_g \Delta c_g \quad (5)$$

3.3 Boundary and initial condition

3.3.1 Liquid Phase:

Initially, there is no CO₂ dissolved in the water,

i.e. for $t=0$, and $(x,y) \in \mathbb{R}^2$

$$\mathbf{v} = \mathbf{u} = c = 0$$

The boundary conditions of the model are:

There is no velocity and flux at boundaries 3 and 4 (see Fig. 3) and at the interface at 1 and 2 the concentration is related to gas pressure according to Henry's law:

$$c = \frac{p_g}{k_H} = \left(\frac{R_B T}{K_H} \right) \times C_g \quad (6)$$

3.3.2. Gas Phase.

Initially at $t=0$,

$$C_g = \frac{p}{R_B T} \quad (7)$$

4. Use of COMSOL Multiphysics

4.1 Conventional form

Numerical modeling of the natural convection model is challenging because high (spatial and temporal) resolution is required in the regions where natural convection takes place. For the liquid phase we apply the creeping flow equation from the fluid flow module and the transport of diluted species from the chemical species transport module. At the interface (see boundary 1 and 2 in Fig 3) a domain probe and distributed ODE are implemented instead of a gas transport equation in the upper region to reduce the computational time. Indeed, high resolution is required in the regions where natural convection takes place, whereas less resolution is required outside the effected region. As the instability moves, we apply an adaptive mesh refinement

for accurately numerically solving the model equations.

4-2 Stream function

Numerical solution of the natural convection problems is somewhat difficult mainly due to stronger coupling that exist between the governing equations. It is often preferred, to express the governing equations of natural convection problems in the stream function-vorticity form, which reduces the number of unknowns.

We define the stream function and the vorticity as follows :

$$v = \frac{\partial \psi}{\partial y}, \quad u = -\frac{\partial \psi}{\partial x} \quad (8)$$

$$\omega = \frac{\partial u}{\partial x} - \frac{\partial v}{\partial y} \quad (9)$$

Following these definitions the governing equation for 2 dimensional natural convection can be written as follows:

$$\nabla^2 \psi = -\omega \quad (10)$$

$$\nabla^2 \omega = -Gr \frac{\partial c}{\partial x} \quad (11)$$

We use also Eq. (4) to describe the transport of CO₂ with the same boundary conditions. Eqs. (10) and (11) are steady state equations and only require boundary conditions. We use that $\psi = 0$ at all boundaries, as there is no flow across these boundaries. In the top boundary we use the symmetry condition see [7], i.e., $\omega = 0$ in Eq. (11). We follow [7] in using the combined conditions that first derivative of the stream in the normal direction is zero and that the second derivative $\partial_{nn}^2 \psi = -\omega$ to represent a no flow condition as a boundary condition for Eq. (11). We use a coordinate transformation to express $\partial_{nn}^2 \psi = -\omega$ in Cartesian coordinates.

4. Results and discussions

Fig 4 shows a numerical simulation using our experimental conditions. It uses 11266 triangular elements, which increases to 22286 in the 18th mesh. The elements are third order for the velocity and second order for the pressure. It uses fifth order Lagrangian elements for the

concentration equation. As can be seen, unstable behavior becomes apparent after 40 seconds.

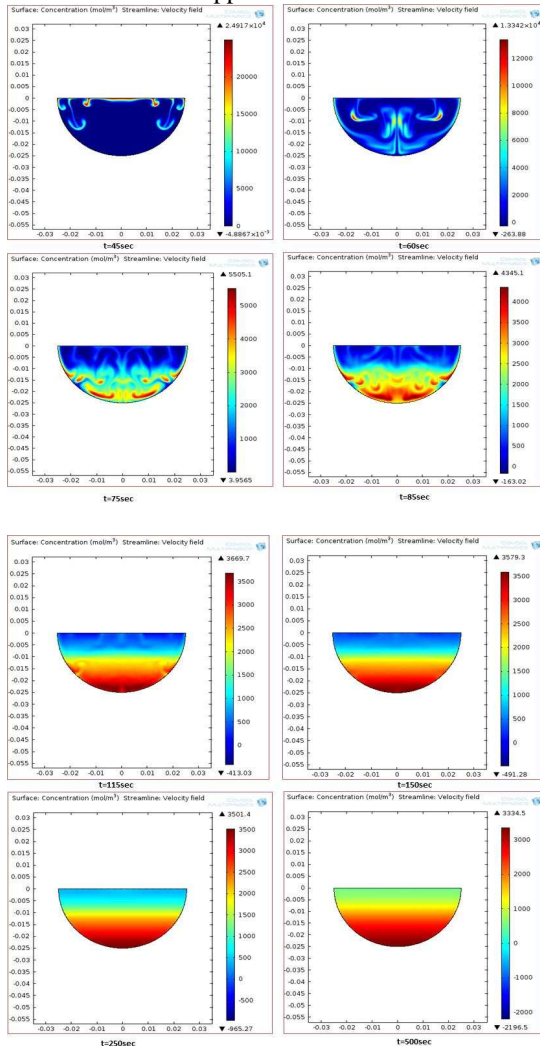


Figure 4: Numerical results of classical model, (See part 4.1)- concentration profile is shown in various times.(t=45,60,75,85,115,150,250 and 500 sec).

. With time, fresh water moves upward and contaminated water with CO₂ goes downward. From t=75 s until t=115s , the concentration profile changes rapidly. The main qualitative correspondence between simulations and experiment is that there is a region of high concentration gradient near the gas-liquid interface. The development of this diffusion layer occurs before natural convection starts. The main difference between the simulations and the experiment is related to the size of the fingers

and the time that they are occurring. The reason for these discrepancies is beyond the scope of this paper.

Conventional numerical simulation shows only six main fingers that start symmetrically on both sides of the center. Numerical simulation does not show any instabilities after 150 seconds, where we observe concentration layers in which amount of CO₂ increases from top to bottom. In comparison to the experimental results, the numerical model shows the onset of natural convection later than the experimental results.

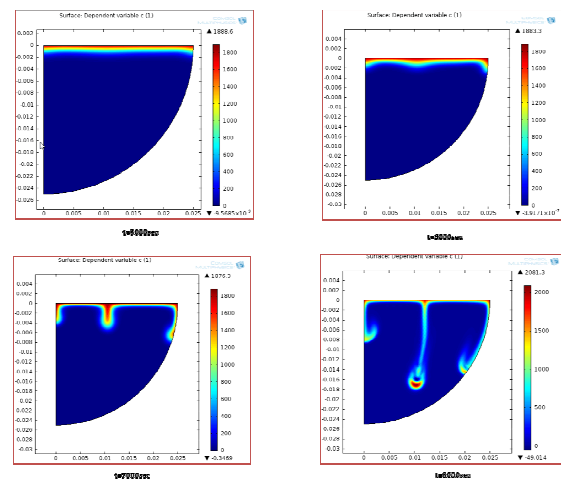


Figure 5: Numerical results of Stream Function model, (See part 4.2)- Concentration profile is shown in various times.(t=5000,6000,7000 and 8000 sec)

Fig 5 indicates numerical results of the Stream Function model. We use fifth order Lagrangian elements and 1156 triangular elements. In comparison with the conventional model and the experiment, the onset of natural convection in the stream function model occurred very late; i.e., around t=6000 sec. In this model, number of fingers is less than in the other results.

5. Conclusions

The main qualitative correspondence between the simulation and the experiment is the existence of a region of high concentration gradient near the gas-liquid interface. The experiments are characterized by extremely narrow fingers, which is a challenge for numerical simulations.

As expected for our preliminary coarse grid results, the wave length of our fingers are much

larger than in the experiments. We also observe that in the simulation the onset of instabilities occurs later than in the experiments. Numerical simulation shows only fingers that start symmetrically on both sides of the center. This indicates that the simulation of experiments requires a denser grid simulation with correspondingly much smaller time step sizes.

6. Nomenclature

c	concentration (mol/m ³)
D	diffusion coefficient (m ² /s)
g	acceleration due to gravity (m/s ²)
k_H	Henry's constant
L	length of the tube (m)
p	pressure (Pa)
Ra	Rayleigh number
T	temperature (K, °C)
t	time (s)
v	velocity in x direction (m/s)
u	velocity in y direction (m/s)
ρ	density of the fluid (kg/m ³)
β_c	volumetric expansion coefficient (m ³ /mol)
μ	viscosity of the fluid (Pa·s)
Gr	Grashof number

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8. Acknowledgements

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