Enhanced transport phenomena in CO2 sequestration and CO2 EOR

Project number: NL23

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The results of this thesis give insight into the (mass)-transfer during flow of gases, especially CO2, in various gas-liquid systems. A number of experiments were performed to investigate the transport phenomena through interfaces with and without surfactant monolayers. The observed phenomena have been incorporated into physical models to predict the fate of CO2 overlaying a bulk liquid or liquid saturated porous media. Moreover, dynamics of (CO2)-foam flow in oil-free and oil-saturated porous media was studied using X-ray tomography. These results are applicable in CO2 sequestration and CO2 EOR projects.

PART I: MASS TRANSFER ASPECTS OF CO2 SEQUESTRATION

The mass transfer of CO2 into liquids was studied in a PVT cell, following the pressure history of a gas phase overlaying a liquid column. It was found that the transfer rate of CO2 into water is significantly higher than predicted from diffusion-based models. By extending the experimental time to a few days we showed that the transfer rate decreases over time and that it is not possible to model the experiments employing Fick’s law with a single (effective)-diffusion coefficient. The short-time and long-time limits of the experiments could be modeled asymptotically to obtain two effective diffusion coefficients. These coefficients are fitting parameters with no physical meaning. The measured effective diffusion coefficients for the short times were two orders of magnitude larger than the molecular diffusivity whereas long-time diffusion coefficients agree with the molecular diffusivity of CO2 in water. It was suggested that at the early stages of the experiments density-driven natural convection enhances the mass transfer of CO2 into water. The results of experiments show that the addition of SDS to water has no measurable effect on the transfer rate at our experimental conditions. A similar mass transfer enhancement was observed for the mass transfer between a gaseous CO2 rich phase with two hydrocarbons (n-decane and n-hexadecane). The effect is less significant for n-hexadecane due to its higher viscosity.

To fully explain the measured pressure trend, a physical model based on density-driven natural convection and diffusion was formulated. The model uses a number of simplifying assumptions, e.g., that Henry’s law is applicable at the interface. Simulation results show that the convective velocity increases until it reaches a maximum and then diminishes gradually as natural convection effects become less important. The maximum velocity corresponds to the time in which the CO2 front reaches the bottom of the vessel. There is a strong correlation between the fluid velocity and the concentration profile with the experimental pressure decline rates. The measured and the theoretically predicted pressure decline in the gas phase agree within the range of experimental errors.

Using the knowledge obtained from bulk liquid experiments, we demonstrated the importance of natural convection for the rate of CO2 storage in aquifers. Initially, the CO2 front moves proportional to the square root of time (diffusion behavior) for different Rayleigh numbers, and then the relationship becomes linear (convection behavior). The time, in which the switching happens, decreases with increasing Rayleigh number. The occurrence of natural convection accelerates the rate of CO2 dissolution. The simulation results show that the non-linear behavior of the flow is strongly dependent on the Rayleigh number. However, as time elapses, the number of fingers decreases due to the decreasing effect of natural convection, similar to the experimental results. This effect can also be observed from the decreasing values of the stream function.
PART II: FOAM FILMS

The mass transfer of gases through foam films is an intriguing problem as two surfactant monolayers interact with each other through surface forces. We chose an Alpha Olefin Sufonate (AOS) surfactant to investigate the effect of different parameters on the transfer rate of gas through foam films. Prior to these experiments, basic properties of AOS solutions and foam films made from those solutions were studied. We showed that, except for salt-free solutions, the addition of salt (NaCl) does not change the adsorption at gas-liquid interfaces of bulk solutions. The thickness of the films remains constant for a concentration range of $c_{AOS} > 0.003$ wt% at a fixed salt concentration of $c_{NaCl} = 0.50$ M. However, the film thickness decreases with addition of NaCl due to the screening of the repulsive forces. The film permeability coefficient, $k$, depends on the permeability and thickness of the film aqueous core and the permeability of the surfactant monolayers. We observed that $k$ increases as the film thickness decreases until a certain value and sharply decreases afterwards. We conclude that beyond that critical point the film permeability is governed by the monolayer permeability, i.e., the adsorption density of the surfactant monolayers, and hence, the decrease of $k$ after this point can be explained by decreased permeability of the monolayers. The film permeability showed an unexpected increase at high surfactant concentrations well above the CMC. We hypothesize that this is a result of faster gas transport via the aqueous film core, facilitated by the micelles. Experiments at different temperatures allowed the energy of the permeability process to be estimated using the simple energy barrier theory.

PART III: FOAM IN POROUS MEDIA

The foaming behavior of CO$_2$ and N$_2$ were compared in natural sandstone cores by means of a CT scanner (X-ray) in the absence and presence of oil. It has been shown that injection of a slug of surfactant prior to CO$_2$ injection can reduce the CO$_2$ mobility, below and above its critical point, when there is no oil present in the medium. In the oil-free porous media, foaming of CO$_2$ builds up a lower pressure drop over the core at both low and high pressures compared to N$_2$. Both gases require a certain penetration depth to develop into foam. The penetration depth is longer for N$_2$ (large entrance effect) and increases with increasing gas velocity. The CT images and calculated water saturation profiles reveal that N$_2$ foam displaces the liquid in a front-like manner (sharp-vertical interface) while the propagation front for CO$_2$ foam is somewhat smeared out at low pressure. Moreover, the ultimate production of N$_2$ foam is always higher than that of CO$_2$ foam. The observed differences in the foaming behavior of the two gases can be related to the differences in their nature, mainly solubility in water, interfacial tensions, pH effects and the possible wettability effects. From these various factors solubility is most likely the most critical one.

At low pressure experiments ($P=1$ bar) injection of N$_2$ after surfactant forms a weak foam when the porous medium is partially saturated with oil. As a result, an oil bank is formed ahead of the foam front and results in additional oil recovery compared to N$_2$ injection alone. CO$_2$ injection, with the same flowrate, does not foam in the core. Above its critical point ($P=90$ bar), no difference was observed between CO$_2$ injection and CO$_2$ foam in terms of recovery and pressure drop over the core. Our experimental results show that injection of surfactant prior to CO$_2$ injection can improve the ongoing CO$_2$-EOR by reducing the gas mobility in the thief zones and diverting CO$_2$ into regions with higher oil saturation. However, it is less likely that CO$_2$ foam itself produces oil from the reservoir.

IMPLICATIONS FOR EOR

This work has the following implications for CO$_2$ storage and CO$_2$ EOR:

- Natural convection effects are favorable for recovery of hydrocarbons because the mixing zone between CO$_2$ gas and the oil becomes longer, which improves the vertical sweep efficiency and the Buckley-Leverett displacement efficiency.
- Permeation of gas through foam films is a strong function of salinity of the water and plays an important role in the efficiency of foam application in Petroleum Engineering.
• Nature of the injected gas plays an important role in the efficiency of foam displacement.
• Foaming of CO\textsubscript{2} above its critical point does not affect the oil recovery.
• Foaming of CO\textsubscript{2} can improve the oil recovery by improving the CO\textsubscript{2} utilization efficiency, i.e., by reducing the gas mobility in the high permeable zones of the reservoir and diverting it into regions with higher oil saturation.