Transport mechanism of CO\textsubscript{2} in fractured chalk

Abstract

The main objective of this study is to develop and test a proper description of diffusion and transport effects in fractured chalk systems with CO\textsubscript{2}, water and oil. Both experiment and numerical modeling work are conducted in this study. Based on the experiments, simulation models are built to mimic the main transport phenomena, including diffusion which was found to be particularly important. The verified modelling framework can properly account for all the relevant forces:

i. viscous displacement
ii. gravity effects
iii. diffusion effects
iv. effects caused by changes in interfacial tension (IFT)

In this study, we have conducted in total of 11 experiments: (a) Work Package (WP) 1-1 and WP1-6 cover CO\textsubscript{2} flooding (CF) into fractured-chalk core saturated with North Sea Chalk Field (NSCF) stock-tank-oil (STO) at zero irreducible-water saturation, (b) first-contact miscibility is studied in WP1-2 for CO\textsubscript{2}-C10 system, (c) WP 2 is the series of IFT measurements conducted on CO\textsubscript{2}-STO system at 110\degree C, (d) WP 3-1 conducts the water flooding (WF) followed by CF at reservoir conditions in a large outcrop chalk with 26 cm long and 12 cm diameter. The fractured-chalk system is initialized with NSCF live-oil and connate-water saturation. (e) WP 4-1 is identical with WP 3-1 except the system is initially saturated with NSCF STO and connate-water saturation. (f) WP 5-1 conducts similar experimental procedure as WP 4-1 in a composite chalk cores, with the total length of 45 cm and average diameter of 3.74 cm. This addresses capillary continuity among all six chalk cores. (g) WP 5-2 is identical to WP 5-1 except the use of synthetic formation water with zero amount of sulfate for the WF instead of sea water with considerable sulfate content. (h) WP 5-3 is identical with WP 5-2 except the use of NSCF reservoir rocks. In all of the experiments, a centralized hole represents the “fracture”.

Prior to above experiments, we develop a constant volume diffusion (CVD) experiments (WP1-7 & WP1-8) for STO and live-oil samples that determine the multi component diffusion coefficients at reservoir conditions. In this technique, the system is initialized with an oil-saturated chalk in direct contact with an overlaying open space filled with CO\textsubscript{2} (CO\textsubscript{2} chamber) at reservoir conditions. Diffusion coefficients are determined by fitting the pressure decline data. Equation-of-state (EOS) is tuned using reported lab PVT data and is employed by numerical simulator. The Parachor parameter in EOS model is further adjusted to match a series of IFT measurements at 110\degree C. The tuned EOS assures a good estimation of IFT, phase behavior and volumetric properties for different mixtures of CO\textsubscript{2} and oil at reservoir conditions.

All experiments are successfully simulated and history matched via numerical modeling by incorporating all the relevant displacement mechanisms. Results shows that active imbibition (strong and moderate type) exists between matrix-fracture space filled with CO\textsubscript{2} (CO\textsubscript{2} chamber) at reservoir conditions. Diffusion coefficients at reservoir conditions. In this technique, the system is initialized with an oil-saturated chalk in direct contact with an overlaying open space filled with CO\textsubscript{2} (CO\textsubscript{2} chamber) at reservoir conditions. Diffusion coefficients are determined by fitting the pressure decline data. Equation-of-state (EOS) is tuned using reported lab PVT data and is employed by numerical simulator. The Parachor parameter in EOS model is further adjusted to match a series of IFT measurements at 110\degree C. The tuned EOS assures a good estimation of IFT, phase behavior and volumetric properties for different mixtures of CO\textsubscript{2} and oil at reservoir conditions.

All experiments are successfully simulated and history matched via numerical modeling by incorporating all the relevant displacement mechanisms. Results shows that active imbibition (strong and moderate type) exists between matrix-fracture system during WF. Moreover, the mass transfer during CF is mainly controlled by diffusion rather than the convective flow or the viscous forces.

Introduction

Conventional recovery mechanisms may not always be successful in naturally fractured reservoirs. High capillary pressures associated with the matrix block coupled with the extreme hydraulic contrast between the matrix and the fractures may result in low recovery efficiencies. Miscible gas (CO\textsubscript{2}) injection may substantially boost the ultimate recovery from those resources. However, modelling of CO\textsubscript{2} injection into fractured oil reservoirs has some significant shortcomings, due to the presence of several complicated transport mechanisms. On top of the viscous displacement and gravity drainage mechanism, CO\textsubscript{2} residing in fractures dissolves in the oil (and in water) residing in the matrix, and the light components in the oil phase are be able to vaporize in to the CO\textsubscript{2}. This would give rise to gradients in the composition, such that further diffusion occurs as well as alterations takes place in fluid properties (such as viscosity, density and IFT changes).

The lack of ability to properly capture those phenomena in reservoir simulation studies makes it difficult to accurately predict
the performance of CO₂ injection in the fractured North Sea chalk reservoirs. Therefore, the main target of this project is to develop a modelling framework, where those effects can be properly accounted for. This can only be achieved by combining the modelling expertise with carefully conducted experimental work stream.

In order to achieve this goal, in total of six work packages are identified, which can be listed as below:

i. WP1: Experiments (core-plug scale) and simulations are conducted to obtain the diffusion coefficients at the reservoir conditions, which can then be utilized subsequent work packages.

ii. WP2: A series of IFT experiments are conducted to describe the IFT variations in the system of CO₂-dead crude oil, which can then be used to fine tune the EOS model.

iii. WP3: Work package contains two experiments (and subsequent simulations) on fractured large-diameter (125mm) chalk samples that constitute an analogue to a real fractured chalk reservoir, with live crude oil, water, and CO₂.

iv. WP4: Work package consists of a single experiment (and subsequent simulations) with a large-diameter (125mm) chalk sample that is identical to WP3 except for the use of dead crude oil instead of live crude oil.

v. WP5: Work package consists of four experiments with 38 mm diameter fractured plug samples. Composite samples with length of approximately 420 mm are used to minimize the capillary end effects.

vi. WP6: Work package utilizes the knowledge gathered in the previous work packages to upscale the work from full core to sector/field scale.

An oil sample was taken from wells from the NSCF reservoirs during a well testing few years ago. Subsequently the samples were sent to the laboratory for utilizing in experimental work. Then we constructed an equation of state (EOS) model of NSCF reservoir, based on historical PVT analysis for utilizing in the simulation studies.

The experiment work started with the first diffusion flow experiments of WP1 in early 2013. WP1 is specifically designed to estimate the diffusion coefficients which can later be utilized in numerical simulation workflow in WP3, WP4, WP5 and WP6. Six out of seven experiments were completed. Results are conducting the modelling work. A good history match has been achieved with the experimental data. All results were presented and discussed during the last technical advisory committee (TAC) meeting in June, 2014 and the subsequent monthly progress update meetings. We provide the detailed experimental and numerical work elsewhere.

Dead oil sample was sent to a Technical University in order to recombine with the synthetic gas to obtain the live crude. A total amount of 5L oil will be recombined which will be utilized in both WP1.8 and WP3. WP1.8 is the only outstanding experiment in WP1 which is specifically designed to estimate the diffusion coefficients between the CO₂ and the live oil components. First batch of the recombined oil (1L) is received to our experimental team Interfacial tension (IFT) tests of WP2 were conducted at the University of Regina in Canada. We provided a technical assistance on the experimental design. The IFTs result has been used by the modelling team to tune the Equation of State (EOS).

**Apparatus and methods**

For projects with experimental work include a description of apparatus and methods here. The experimental work is conducted in two rigs, one that is used for the experiments on 38 mm diameter samples, and one that is used for the experiments on 123 mm diameter samples. The first rig, identified as “the Reservoir Conditions Rig”, has been in use for several years. The second rig, identified as “the Full Core Rig”, has just been constructed. Table 1 gives some specifications for the two rigs. Figure 1 shows a photo of the Reservoir Conditions Rig. Both rigs utilize hydrostatic core holders for the rock samples. In both rigs the core holder, pressure vessels with injection fluids, densitometer, and the viscometer are placed within an oven with air recirculation that ensures a stable and homogeneous temperature distribution. Both rigs have 3-phase acoustic separator placed outside the oven that receives and quantifies the produced fluids. The acoustic separators are operated at ambient laboratory temperature, 22 to 26°C, and a pressure between 1 and 10 bara. Both rigs are equipped with a densitometer that measures the density of the produced fluid. The Full Core Rig is equipped with a viscometer that shall be used for determining the viscosity of stock tank oil and live oil at reservoir conditions.

**Table 1 Specifications of equipment**

| Reservoir rig | Full core rig |
|--------------|--------------|
| Pressure rating | 690 bar | 690 bar |
| Max. temperature | 120°C | 120°C |
| Temp. stability | 0.5°C | 0.5°C |
| Flow rate | 0.01 - 500 ml/h | 0.01 - 500 ml/h |
| Flow accuracy | 1% of nominal rate | 1% of nominal rate |
| Pressure accuracy | 0.5 bar | 0.5 bar |
| Separator | 3-phase acoustic | 3-phase acoustic |
| Separator accuracy | 1 ml | 4 ml |
| Sample diameter | 38 mm | 123 mm |
| Sample length | max 45 cm | max 30 cm |
| Sample orientation | Vertical or horizontal | Vertical |
| Vessels for injection fluid | 1 liter | 5 liter |
| Additional equipment for reservoir conditions | Densitometer, 2-phase separator | Densitometer, Viscometer |

**Figure 1** The Reservoir Conditions Rig equipped with the core holder to be used in WP5.
All experiments are conducted with logging of all rig equipment, typically with logging interval 1 minute.

Two EOS models with 41 single carbon number components were developed to match the PVT data; one EOS model for 268°F (SCN41-268F) and the other for 90°F. Both EOS models capture the critical transition correctly and give good description of single phase and two phase PVT measurements. The EOS model for 268°F will be used in the compositional numerical model and to reduce the CPU time and memory storage a “pseudoized” 10 component EOS based on SCN41-268F was developed. Figure 2 shows the new pseudo-components from existing SCN components.

Figure 2 Pseudo-components list.

ECLIPSE 300 2012.1 version is the commercial compositional numerical simulator used in this project. This simulator has both concentration driven and chemical-potential driven diffusion option. The modelling work is done using the latter option due to its ability to capture complex phase behaviour during diffusion. The numerical model is a 2-dimensional radial grid, run with Fully Implicit solution procedures (for the stability). In ECL300, the oil and gas phase diffusion coefficients for each component are needed as the input data. These values were calculated using extended Sigmund correlation by da Silva and Belery, which later tuned to match the experimental data.

Fracture is modelled by using grid blocks along z-direction, a zero capillary pressure, 100% porosity, and high permeability were assigned for the fracture grids. Figure 3 shows the general workflow for the modelling work. The grid sensitivity was done to ensure converged solutions. The fracture permeability sensitivity work was done to find a fracture permeability value that is close to infinite as possible without having impact on the results and/or numerical stability. Please refer to Figure 4 & 5 for example results from this work.

Figure 3 Modeling workflow.

Sample selection and sample preparation

If samples are used in the project then include a description of used samples and the preparation of the samples for the experimental work. Because of scarcity of full core samples of reservoir chalk it was decided to conduct most of the experiments on outcrop chalk. After a screening of potential sample localities it was decided to use sample material from the Sigerslev Quarry on Stevns, Sjaelland, which provides very homogeneous chalk from the Tor Formation with porosity between 45 and 51%, and klinkenberg permeability between 2.5 and 6 m D. All rock samples undergo thorough cleaning followed by poroperm characterization prior to the experiments of the work packages.

Experimental work

For projects with experimental work include a description of the experimental work.

Results and deliverables

Work package (WP) 1 consists of in total seven reservoir conditions (high temperature and pressure) experiments. In all those experiments, CO₂ is flooded via the fracture system and interacts with the fluids residing in the matrix. We have completed six of those experiments and subsequent simulations were run for history matching purposes.
A brief description of those experiments is listed as below:

i. WP 1.1 – System is initially 100% saturated with dead oil. The sample contains an axial hole with diameter 6 mm that supplies the functionality of a fracture.

ii. WP 1.2 – System is initially 100% saturated with laboratory oil (same density as CO$_2$). nC10 was utilized as the model oil, which is found to be at the same density as CO$_2$ in reservoir conditions. The sample contains an axial hole with diameter 6 mm that supplies the functionality of a fracture.

iii. WP 1.3 – System is initially 100% saturated with water. The sample contains an axial hole with diameter 6 mm that supplies the functionality of a fracture.

iv. WP 1.4 – Core plug is replaced with a phantom to perform a blank experiment to study the diffusivity of the rubber sleeve wrapped around the core plug/phantom.

v. WP 1.5 – System is initially 100% saturated with water and $S_{ro}$ . This experiment was later decided to be removed from the program (during the TAC meeting in December, 2013) due to the difficulties associated with the modeling of three mobile phases.

vi. WP 1.6 – System is initially 100% saturated with dead oil. This experiment is a repetition of WP 1.1. Core plug is wrapped with metal foil in order to avoid CO$_2$ diffusion into the annulus. The sample contains an axial hole with diameter 6 mm that supplies the functionality of a fracture.

vii. WP 1.7 – Constant volume diffusion experiment. This experiment was added to program during the TAC meeting held in December, 2013. The sample is not fractured.

viii. WP 1.8 – Constant volume diffusion experiment. This experiment was added to program during the TAC meeting held in December, 2013. This experiment is same as WP 1.7, however live oil is utilized in WP1.8. The sample is not fractured.

We obtain excellent matches between the experimentally measured recovery profiles and the numerically predicted ones. This suggests that the modeling workflow incorporates a representative EOS model and all the underlying recovery mechanisms (including the diffusive flux) are being properly accounted for. See Figures 6 & 7, which compares the experimentally measured data with the numerically generated ones.

**Interpretation and discussion**

On the first phase of project, the main focus of the project was on the WP1. In WP1, experiments are conducted to obtain CO$_2$ diffusion coefficients in North Sea chalk at the reservoir conditions. Once the experiments are conducted, simulation models are generated which mimics the experimental conditions as closely as possible. Runs are then conducted to regenerate the experimental data by tuning the oil and gas diffusion coefficients which are input parameters for running the simulations. A brief discussion on some of those experiments and simulations is below.

Table 2 & Table 3 summarize experimental parameters as well as the ones used during the simulations. Note that parameters are chosen as closely as possible to the experimental data. In WP1.2, system is saturated with n-decane (C10) in order to minimize the density difference between the CO$_2$ injected via the fracture and the oil residing in the matrix. The axial hole through the sample causes the pressure difference between sample inlet and outlet to be close to zero. With only minor density contrast between the fluid phases, the convective and viscous effects are minimized, and the displacement is expected to be dominated by diffusion. A very good match between the experimental data and simulation is obtained by implementing a diffusion coefficient of 1.0-0.01 cm$^2$/hr. Note that the results are insensitive to the vertical permeability of the system which suggests that the displacement is indeed dominated by the diffusion rather than convective flux or viscous forces.

In WP1.6, system is saturated with the NSCF stock tank oil (STO). CO$_2$ is then injected via the inlet at the top of the fracture and the oil is produced at the outlet at the bottom. The axial hole in the sample causes the pressure difference between sample inlet and outlet to be close to zero. An excellent match between the experimental data and simulation results suggests that model is capable of honoring the right displacement physics (see Figure 6). Set of diffusion coefficients used in the matched model is presented in Table 4.

In WP1.7, a so-called constant volume diffusion experiment is conducted. A schematic and a photo of the core holder can be seen in Figure 8. A numerical model is generated to mimic the system (Figure 9). CO$_2$ is injected at inlet on the top until it reaches a certain volume (26.54ml) to fill the fluid chamber on the top of the core holder (Figure 10). Then the injector and producer are shut in to let diffusion take place. Once the CO$_2$ diffuses into the STO, we observe a reduction on pressure which can be used to predict the diffusion coefficients. See the very good match obtained between the experimentally measured and numerically modeled data (Figure 7). Set of diffusion coefficients used in the matched model is presented in Table 5.

It should be noted that WP 1-6 and WP 1-7 have different experimental set-up. The fluid pressure is held constant in WP 1-6, while decreasing fluid pressure due to diffusion exist in WP 1-7. As we know, the diffusion coefficient is a pressure dependent parameter. In WP 1-7 the recovery mechanism mainly controlled by diffusion. While in WP 1-7, the recovery is driven by gravity forces, viscous forces, and diffusion. Thus, a mismatch diffusion coefficient obtained from WP 1-6 and WP 1-7 is reasonable. Results suggest that we are able to successfully predict the dynamic fluid properties via the EOS model as well as the diffusion coefficients through our numerical modeling approach. Hence, the predicted diffusion coefficients can be implemented in the subsequent work packages of this project.

An important shortcoming while assigning diffusion coefficients is reservoir simulators assume no compositional dependency on diffusion. However, in a gas injection process the composition of the injected gas and oil continuously alters due to the component exchange via the vaporizing and condensing gas drive processes. Hence, the diffusion coefficients do also change during the displacement process. See the oil diffusion coefficients predicted via the extended Sigmoid correlation in Figure 11. Note that it is significantly affected by the amount of CO$_2$ dissolved in the system. Our Results for other work in WP2 through 6 are presented elsewhere. \(^3\)\(^7\)
Table 2 Experimental data and input parameters for the numerical model in WP1.1 and WP1.6

| Parameter                                    | WP1-1 Lab Data | WP1-1 ECL300 Model | WP1-6 Lab Data | WP1-6 ECL300 Model |
|----------------------------------------------|----------------|--------------------|----------------|--------------------|
| Matrix pore volume (ml)                      | 38.05          | 38.06              | 37.53          | 37.58              |
| Volume of central hole (ml)                  | 2.13           | 2.13               | 2.08           | 2.08               |
| Core porosity (fraction)                     | 0.468          | 0.468              | 0.4689         | 0.468              |
| Core permeability (mD)                       | 4.9            | 4.9                | 2.47           | 2.5                |
| Fracture permeability (mD)                   | -              | 5000               | -              | 10000              |
| Annulus porosity (fraction)                  | 1              | 1                  | -              | -                  |
| Porosity of the rubber sleeve (fraction)     | -              | 0.01               | -              | -                  |
| permeability of the rubber sleeve (mD)       | -              | 0.0                | -              | -                  |
| Annulus permeability (mD)                    | -              | 5000               | -              | -                  |
| DIFFMR- at left-face of the sleeve           | -              | 0.015              | -              | -                  |

Table 3 Experimental data and input parameters for the numerical model in WP1.2.

| Parameter                                    | WP1-2 Lab Data | WP1-2 Model 1-2 |
|----------------------------------------------|----------------|-----------------|
| Number of grid (Nz,N0,Nz)                    | 1              | 50,1,50         |
| Core pore volume (ml)                        | 38.01          | 37.95           |
| volume of central hole (ml)                  | 2.12           | 2.12            |
| Core porosity (fraction)                     | 0.417          | 0.471           |
| Core permeability (mD)                       | 2.6            | 2.6             |
| permeability of rubber sleeve(mD)            | -              | 0.0             |
| Fracture of permeability                     | -              | 5000            |

Table 4 Diffusion coefficient used in WP 1-6

| Component (cm²/hr)                           | N2-C1 | CO₂ | C2  | C3  | C4-C5 | C6  | C7-C12 | C13-C20 | C21-C35 | C36+  |
|----------------------------------------------|-------|-----|-----|-----|-------|-----|--------|---------|---------|-------|
| DIFF-Gas                                     | 1.081 | 0.232 | 0.699 | 0.538 | 0.422 | 0.357 | 0.270 | 0.183 | 0.122 | 0.093 |
| DIFF-Oil                                     | 0.271 | 0.162 | 0.174 | 0.133 | 0.102 | 0.085 | 0.053 | 0.046 | 0.035 | 0.027 |

Table 5 Diffusion coefficient used in WP 1-7

| Component (cm²/hr)                           | N2-C1 | CO₂ | C2  | C3  | C4-C5 | C6  | C7-C12 | C13-C20 | C21-C35 | C36+  |
|----------------------------------------------|-------|-----|-----|-----|-------|-----|--------|---------|---------|-------|
| DIFF-Gas                                     | 0.011 | 0.003 | 0.007 | 0.006 | 0.004 | 0.004 | 0.003 | 0.002 | 0.001 | 0.001 |
| DIFF-Oil                                     | 0.136 | 0.081 | 0.087 | 0.067 | 0.051 | 0.043 | 0.027 | 0.023 | 0.017 | 0.014 |

Figure 6 Cumulative oil production versus time for assigning zero vertical permeability. Also current match is compared (WP1-6).

Citation: Ghasemi M, Astutik W, Alavian S, et al. Transport mechanism of CO₂ in fractured chalk. Int J Petrochem Sci Eng. 2018;3(3):80-86. DOI: 10.15406/ipcse.2018.03.00080
Figure 7 Pressure decay versus time. Performance of the model against data WP1-7.

Figure 8 The shape of core-holder used in WP 1-7.

Figure 9 The numerical model used to model the experiment.

Figure 10 The dimension of the core holder used in WP1-7 experiment. It shows two regions. The pink region is CO2 chamber and there orange region holds the chalk core for the CVD test experiment.

Figure 11 Multi component diffusion coefficients determined by modified Sigmund correlation.

Conclusion and recommendations

Some important conclusion as well as the suggested future recommendations can be found below:

i. WP1 is nearly complete. Only one outstanding experiment is left which will be initiated shortly.

ii. WP2 is completed. IFT measurements conducted in University of Regina are in good agreement with the currently utilized EOS model.

iii. A set of reservoir condition (high T&P) experiments were conducted and successfully history matched by accounting for all the underlying flow mechanisms including the diffusive flux.

Citation: Ghasemi M, Astutik W, Alavian S, et al. Transport mechanism of CO$_2$ in fractured chalk. Int J Petrochem Sci Eng. 2018;3(3):80-86.
DOI: 10.15406/ipcse.2018.03.00080
iv. We are able to successfully predict diffusion coefficients in reservoir conditions, which can then be utilized in WP’s 3-6.

v. We also successfully conducted the experimental and numerical work for a composite core saturated with STO, a large diameter core saturated with live-oil and STO, (WP2 though 6).

Nomenclature
Include applied nomenclature. Use preferentially SPE’s nomenclature.

Acknowledgements
We would like to thank Joint Chalk Research (JCR) consortium for permission to publish this work and providing financial support of this study and series of other CO₂ EOR research projects in the North Sea. JCR consortium consists of Norwegian Petroleum Directorate (NPD), Danish Energy Agency, the Danish North Sea Fund, BP, ConocoPhillips, DONG, ENI, Hess, Maersk Oil, Shell, Statoil, and Total.

Conflict of interest
The author declares that there is no conflict of interest

References
1. Any document etc. used as reference. Reference to be numbered (1, 2, 3 etc.) and the number be used in the text as a reference to the reference.
2. Da Silva FV, Belery P. Molecular Diffusion in Naturally Featured Reservoirs: a Decisive Recovery Mechanism. 64th SPE Annual Technical Conference and Exhibition; 1989 October 8-11; Texas, USA.
3. Ghasemi M, Astutik W, Alavian SA, et al. Tertiary-CO₂ Flooding in a Composite Fractured-Chalk Reservoir. J Pet Sci Eng. 2018;160:327–340.
4. Ghasemi M, Astutik W, Alavian SA, et al. Determining Diffusion Coefficients for Carbon Dioxide Injection in Oil-Saturated Chalk by Use of a Constant-Volume-Diffusion Method. SPE Journal. 2017;22(2):505–520.
5. Ghasemi M, Astutik W, Alavian SA, et al. Experimental and Numerical Investigation of Tertiary-CO₂ Flooding in a Fractured Chalk Reservoir. J Pet Sci Eng. 2018;164:485–500.
6. Ghasemi M, Astutik W, Alavian SA, et al. Laboratory Tests and Modeling of Carbon Dioxide Injection in Chalk with Fracture-Matrix Transport Mechanisms. Society of Petroleum Engineers. 2018;21(1):122–136.
7. Ghasemi M, Astutik W, Alavian SA, et al. Impact of Pressure on Tertiary-CO₂ Flooding in a Fractured Chalk Reservoir. J Pet Sci Eng. 2018;167:406–417.