**CO₂ Solubility Characteristics of Crude Oils related to Carbon Capture and Utilization (CCU)**

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Carbon Capture and Utilization (CCU) has been focused in the world to reduce not only CO₂ emissions but also economical cost especially in fossil fuel energy sectors. The Laboratory of Mineral Resources Production and Safety Engineering (REPS), Kyushu University, has investigated physical properties and operation systems of the CCU, especially Enhanced Oil Recovery (EOR) and Enhanced Coal Bed Methane Recovery (ECBM). In this review, enhanced cold oil recovery has been introduced as one of CCU applications using immiscible CO₂ gas. The swelling factors of heavy and intermediate crude oils with CO₂ gas dissolution were measured in a cell which pressure was less than 10 MPa at expected oil reservoir temperature of 50 °C. The swelling factor increased with increasing CO₂ pressure. In CO₂ supercritical phase, gas diffusion coefficients in oil was almost twice as high as those in gas phase. From observation of oil drainage tests using sandstone cores, gas dissolution in the oil does not make a clear effect on oil mobility; however foamy oil, included CO₂ micro bubbles generated by depressurization, induced oil drainage from the oil saturated core.

1. Introduction

Carbon Capture and Storage (CCS) or Utilization (CCU) are expected to be powerful tools to reduce CO₂ emissions to the atmosphere from large scale sources, such as electric power, oil refinery, steal making, cement plants, with continuing their activities Those contain the CO₂ separation or capture from flue gases at the plants and the transport and injecting CO₂ into oil and gas reservoirs, and coal seams. Those technical operations have been accumulated in petroleum industry. Recently, CCU has been popular rapidly, since it can cover economic investments and operation costs by producing variable fuels (Verland der Chemishen Industries, 2009). It has been applied to fossil fuel productions using CO₂, such as Enhanced Oil and Gas Recovery (CO₂-EOR and EGR), Enhanced Coal Bed Methane (CO₂-ECBM).

The cold oil productions by injecting CO₂ into oil reservoirs have been investigated. When the oil is produced with injecting captured CO₂, the produced oil is expected to be 70% ‘Carbon-free’, because it can be evaluated from difference between the carbon content in the incremental oil produced and volume of CO₂ left in the reservoir. A next generation CO₂ storage technology can produce 100% ‘Carbon-free’ oil (Phares, 2008). When injecting CO₂ or CH₄ into oil reservoirs, the oil swelling coefficient and gas diffusion coefficient in the oil phase are important parameters to carry numerical simulation of cold oil production. The interfacial tension and swelling are usually measured in parallel, and used to evaluate the diffusion coefficient.

Dissolution of soluble gas contributes to cold oil production, as it reduces oil viscosity and capillary pressure. It also causes swelling of the oil, which increases oil saturation in reservoir pore space and subsequently the relative permeability of the oil. Measurements of gas diffusion and dissolution behavior in crude oils are required, since gas dissolution is expected to make increase of oil mobility in reservoirs. These oil mobility changes can be used for cold production by understanding drainage mechanisms.

The Laboratory of Mineral Resources Production and Safety Engineering, Kyushu University (REPS) has been measured basic CO₂ characteristics in oil, coal, rocks and coal reservoirs. In this review, measurement results of CO₂ solubility and swelling factor in oils have been presented in order to propose EOR operations by foaming CO₂ micro bubbles in the oil.

2. Measurement Apparatuses and Procedures

2.1 Crude Oil Samples and Sandstone Core

Two dead oil samples of intermediate and heavy were used for present measurements. The heavy oil was produced in Japan and had the following parameters: API-gravity = 11.5; viscosity = 821 mPa·s @30 °C. The intermediate oil was produced in Oman and had the following parameters; API-gravity = 29.3 and viscosity = 9.7 mPa·s @30 °C.

The Berea sandstone cores with 25.4 and 38.1 mm in diameter and 50 and 70 mm in length were prepared and used for measurements. The cores were saturated with heavy oil by oil flooding from an end surface after water saturation, however, very fine pores were not saturated completely with oil. The core was placed in the high pressure cell to measure gas solubility and oil drainage amount from the core. Following properties were examined; oil saturation = 77.1%, water saturation = 22.9%, bulk volume = 54.3 cm³, porosity = 21.0% and absolute permeability = 500 to 600 mD.

2.2 High Pressure Cell for Swelling Measurements

A high-pressure cell with two visualization windows was used for the measurement of oil swelling and diffusion coefficient for CO₂ gas (see Fig. 1). Maximum pressure

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and temperature of the cell were 10 MPa and 95 °C, respectively. Hot water in a water bath kept constant temperature by a thermostat was circulated through two jackets around the cell, and used to maintain a constant temperature (50°C) in the pressure cell covered with thermal insulation.

Oil swelling was evaluated by photography of the surface movement of the oil column, and then visual inspection of the photographs. The surface movement was generated with gas dissolution in the oil columns. Swelling-time curves were constructed to estimate the diffusion coefficients in the oil from the unsteady diffusion equation. Approximately 2g oil was placed in the column, and the mass of the oil was recorded before the measurements. It was taken few weeks to measure gas dissolution in oil, especially heavy one.

2.3 PVT Measurements for CO₂ Gas Dissolution

Accurate CO₂ phase behavior and gas solubility in liquid are essential parameter for proper management of CO₂ injection into reservoirs. Fig. 2 shows the PVT apparatus (RUSKA Model 2370) used for present measurements. The volume in the pump cell was changed independently with moving a piston by a computer-controlled servo motor. A set of data consisting pressure, volume and temperature in the cell was recorded continuously every 10 s. The stainless steel cylinder was used for the PVT pump cell. They were vertically mounted in the temperature-controlled air bath. The maximum properties of the pump cell are pressure = 70 MPa, temperature = 200 °C, cell volume = 360 ml.

3. Measurement Results and Discussion

3.1 Swelling Factor-Time Curve

In this study, a unit ratio of oil swelling factor, \( R(t) \), before equilibrium dissolution is defined against elapsed time t(s) as:

\[
\dot{R}_s(t) = \frac{(S_f(t) - 1)}{(S_f^\infty - 1)}
\]

where \( S_f^\infty \) is the swelling factor at equilibrium condition. The unit ratio-time curve, \( R_s(t) \), shows almost cumulative gas dissolution in the crude oil vs. elapsed time. Fig. 3 shows generalized plots in unit ratio of swelling factors, \( R_s(t) \), of the heavy oil. The progress of oil swelling with time is closely related to cumulative gas diffusion amount of gas into the oil.

Oil swelling factors of the intermediate oil with CO₂ were larger than those of the heavy oil, while the diffusion time to reach equilibrium of gas dissolution in the heavy oil needed 30 times longer than that of the intermediate oil.

3.2 Oil Swelling Coefficient

The swelling factor at equilibrium less than bubble point pressure is assumed to be proportional to the pressure and is defined as:

\[
\dot{S}_f = 1 + f_{sw} \cdot P
\]

where \( f_{sw} \) is a proportional constant to pressure which is defined as swelling coefficient in this study. The swelling coefficient depends on characteristics of oil and gas.

The swelling factors of heavy and intermediate oil samples were measured with increasing gas pressure as shown in Fig. 4. These results show that the swelling coefficient of CO₂ in the intermediate oil is approximately 1.8 times higher than that of the heavy oil for pressure range up to 7.8 MPa. There was no apparent change in the relationship between pressure and the swelling factor before and after the supercritical pressure around 8 MPa, thus CO₂ dissolution and oil swelling were not so sensitive at pressure less than 10 MP.
3.3 Gas Solubility of Crude Oils

The relationship between gas dissolution and the oil swelling may be proportional, since it is assumed that the gas molecules in the oil phase are existed like in its liquid phase with limited movements, when gas dissolution occurs in the oil.

The PVT measurement results of gas solubility for CO₂ and CH₄ by are plotted in Fig. 5. The gas solubility $C_s$ (mmol/g) can be estimated from the swelling factor, $S_{fw}$, using the following empirical equation based on the measurement results as shown in Fig. 6 without difference of CO₂ and CH₄:

$$C_s = 38.1(S_{fw} - 1). \quad (3)$$

Fig. 5 CO₂ and CH₄ solubility measured by the PVT.

3.4 Gas Diffusion Coefficient in Oils

The unit-ratio of oil swelling factor $R_s(t)$ is a function of the diffusion coefficient in oil $D$ (m²/s), oil column length $L$ (m) and time $t$ (s). As shown in Fig. 7, values of $D$ were evaluated based on the measured swelling-time curve fitting with following analytical solution:

$$R_s(t) = 1 - \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n-1)^2} \exp\left(-D\lambda_n^2 t\right) \quad (4)$$

where $\lambda_n = (2n-1)\pi/(2L)$ (1/m).

The CO₂ gas diffusion coefficient in the intermediate oil was 50 to 80 times higher than those of the heavy oil. In both of oils, the diffusion coefficients increased slightly with the pressure in CO₂ gas phase. However, the CO₂ gas diffusion coefficients in supercritical CO₂ phase were more than twice as high as those in the gas phase.

The empirical equation between $D$ (m²/s) and API-gravity has been presented by Kono et al. (2011) based on the present results and the results of Athabasca bitumen measured by Upreti and Mehrrotra (2002):

$$D = 2.9 \times 10^{-11} \exp(0.247 \times API) \quad (5)$$

4. Heavy Oil Drainage by Generating Foamy Oil

Oil drainage tests were conducted in the high pressure cell at 50°C by observing heavy oil drainage from oil saturated cores by applying CO₂ dissolution and depressurization. The core was placed for 6 hours in the high pressure cell where 10 MPa and 50°C CO₂ gas was injected to form a saturated CO₂ dissolution in oil saturated in the core. The oil drainage from the core surface was not observed on dissolution process, thus the oil in sandstone pores was in stable and not drained by drops of oil viscosity and surface tension due to CO₂ dissolution, while it was clearly observed on the depressurization process with pressure gradient of 0.037 MPa/min from 10 MPa. As shown in Fig. 8, foamy oil was drained which was observed on the core surface from the pressure less 4 MPa. This shows that foamy oil including CO₂ micro bubbles contributed to heavy oil drainage.
from the core (Mastman et al., 2001). For an example, Huff and Puff operation with CO₂ gas pressurization and depressurization cycle can be applied for cold heavy oil production.

Fig. 8 Heavy oil drainage from oil saturated core (center) and microscope photo of foamy oil (right).

5. Conclusion

In this review on Carbon Capture and Utilization (CCU), the measurement results of CO₂ gas solubility and related swelling of crude oils have been introduced. Furthermore, the enhanced heavy oil production method has been proposed by generating foamy oil including CO₂ micro bubbles by an operation of depressurization.

References