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Determination of diffusion coefficients of supercritical CO_2 under tight oil reservoir conditions with pressure-decay method

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ABSTRACT

A generalized methodology has been developed to determine the diffusion coefficients of supercritical CO_2 under tight oil reservoir conditions considering the oil swelling effect. Experimentally, a diffusion cell has been used to perform diffusion tests for CO_2 in tight formation cores, saturated with crude oil, under different pressure and temperature values. The dynamic pressure-decay curves of CO_2 in the annular space of the diffusion cell were monitored and recorded during the measurements. Theoretically, the Peng–Robinson equation of state (PR EOS) with a modified α function has been incorporated to develop a one-dimensional radial diffusion model for the CO_2–tight formation core systems. Also, the crude oil sample has been characterized as three pseudo-components for the accurate prediction of phase behavior of the CO_2 and crude oil system. The CO_2 diffusion coefficients, under different pressure and temperature values, were determined once the discrepancy between the measured and the calculated times, under the same pressure decrease of the diffusion process was minimized. According to the CO_2 concentration profiles in the cores, the diffusion process is divided into two distinct parts, i.e., the early stage, characterized by the fast diffusion rate, and the later stage with the slow diffusion rate. While the pressure and the temperature increase, the CO_2 diffusion coefficient initially increases quickly and then reaches a plateau. Lower viscosity of crude oil, higher temperature, and higher pressure facilitate the diffusion of CO_2 into the crude oil, under tight formation conditions.

1. Introduction

Since the 1950s, numerous studies and applications have shown that CO_2 can be an ideal agent for enhancing oil recovery (EOR) of the light-, medium-, or even heavy-oil reservoirs [1–7]. Many CO_2 EOR projects have been conducted in the USA, Canada, China, and other countries, including immiscible CO_2 flooding, miscible CO_2 flooding, and CO_2 huff-n-puff processes. According to the survey, gas-driving projects accounted for 54% of global EOR projects in 2012. There are 77% projects in total related to CO_2 gas-driving, which proves the important role of CO_2 in oilfield development [8]. It is worthy to be mentioned, that CO_2 EOR methods not only increase oil recovery, but also mitigate the greenhouse gas emissions, by storing CO_2 in depleted reservoirs. It is estimated that CO_2 EOR methods have the potential to recover 1.07 trillion barrels of oil and store 320 billion tons of CO_2 in the basins worldwide [9]. The commonly recognized CO_2 EOR mechanisms include oil viscosity reduction, oil swelling effect, interfacial tension (IFT) reduction, and light-hydrocarbons extraction by supercritical CO_2 [10–12]. For low permeability reservoirs and tight oil reservoirs, water flooding is hard or impossible to be performed due to the high injection pressure, thus CO_2 EOR methods are indispensable. Diffusion phenomenon exists in both CO_2 flooding and CO_2 huff-n-puff process, it is fundamentally and practically important to study the mass transfer of CO_2 under reservoir conditions, so that we can better understand and quantify the underlying mechanisms of CO_2 EOR and predict the effect of above methods precisely.

According to Fick's diffusion law, the gas diffusion process is characterized with the diffusion coefficient. It is defined as the amount of gas that goes through a unit area per unit time under a unit concentration gradient [13]. The diffusion of CO_2 in crude oil, under bulk or porous media conditions, is a spontaneous process where the mass transfer of CO_2 is controlled by concentration difference. The diffusion is influenced by several factors, such as temperature, pressure, oil saturation, water saturation and formation permeability. The available methods of measuring diffusion coefficient can be classified into two types: the direct measurement method and the indirect measurement method. The direct measurement method gets the dissolved gas concentration in liquids under specific conditions directly, and then determines diffusion coefficient through Fick's diffusion law. Nuclear magnetic resonance (NMR) method [14–17], X-ray Computer-Assisted

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Tomography (CAT) method [15,18,19] and sampling analysis method [20,21] are representative in this kind of method. For the indirect measurement method, the oil property change due to gas diffusion is observed, which is a function of time and concentration of the dissolved gas [22–29]. Through the correlation between the properties of crude oil and the amount of dissolved CO_2, the process of CO_2 diffusion can be predicted, and the diffusion coefficients can be calculated via Fick's law. Pressure-decay method [22–24], Dynamic Pendant Drop Shape Analysis (DPDSA) [25,28,29] and dynamic volume analysis [26,27] are commonly used in this kind of method. Although the above two methods are theoretically feasible, each has its defects. The former method utilizes the gas concentration profile to determine the parameters, however it is difficult to sample in porous media to measure gas concentration for sampling analysis. Moreover, NMR is a common technique in such situation but it is not cost efficient. The latter method determines the parameters by measuring the properties of crude oil or of a pressure-volume-temperature (PVT) system. The experiment part is easy to operate, while a complex correction process is required to convert the experiment data into the final accurate value of diffusion coefficient.

According to the fluids distribution pattern, gas diffusion can be divided into two categories. One is the gas diffusion process in bulk liquid phase, consisting of brine, dead oil, and live oil. Its mathematical model is relatively simple and an analytical solution can be obtained [29–33]. Coupling heat and mass transfer of a gas mixture–heavy oil system, at high pressures and elevated temperatures, has been researched with PVT test and numerical method [22–24]. The other gas diffusion process occurs in porous media saturated with brine or oil, under reservoir conditions [34–37]. Due to the complex structure of the porous media, which is called tortuosity, the transport path of CO_2 in crude oil is irregular, and the diffusion process is slowed down. In addition, the dissolved CO_2 in brine or crude oil can cause swelling effect, which leads the fluids to move to opposite direction than that of the diffusion. There is clear dependency between diffusion and swelling effect in a porous media, thus a velocity term is added to the partial differential equation. The mathematical models of diffusion in porous media are solved by numerical methods [36,37]. The CO_2 diffusion coefficient is an important input parameter for the large-scale modeling and simulation of carbon capture and storage (CCS) or CO_2-EOR. However, most of the existing results are for the diffusion in bulk phase [22–25,27–29], and few studies of the CO_2 diffusion coefficient in tight oil reservoirs are available. Thus, we do not have sufficient information about the effects of temperature and pressure on the CO_2 diffusion, under tight oil reservoir conditions.

In this study, a generalized methodology has been developed to determine mass transfer from supercritical CO_2 to tight formation cores, saturated with crude oil at different pressures and temperatures. Theoretically, the Peng–Robinson Equation of State (PR EOS) [38] and the mass conservation equation have been developed to describe the mass transfer from CO_2 to crude oil in tight formation cores, at high pressure and elevated temperatures. Experimentally, the decaying pressures of the CO_2 phase in the annular space of the diffusion cell are measured during the mass transfer process, under a constant temperature. The diffusion coefficient of CO_2 in porous media is determined once the discrepancy between the measured and calculated pressure-decay curves, during the diffusion measurement, has been minimized. Also, the concentration profile and the velocity profile in the porous media are correspondingly determined.

2. Experimental section

2.1. Materials

The light oil, collected from the Changji Oilfield in Xinjiang Province, China, is cleaned with centrifuge process to remove any sand particles and brine. Changji Oilfield is a tight oil reservoir, where its depth is 3270 m. The density and the viscosity of the cleaned crude oil are measured, using a densitometer (model DMA 4200M, Anton Paar, Austria) and a viscometer (model DV-II + , Brookfield, USA), respectively. At atmospheric pressure, and temperature 50 °C, the density is 864.2 kg/m^3 and the viscosity is 7.26 mPa s, and the viscosity-temperature curve of the oil is given in the Appendix A1. Using the standard ASTM D2007-03 method and filter papers with a pore size of 2.5 μm, the asphaltene content of the cleaned light oil is measured to be 0.71 wt% (n-heptane insoluble). The compositional analysis of the dead oil is presented in Table 1. It is found that heavy components of C_{20+} are only 21.29 mol%, resulting in low density and low viscosity. This light crude oil contains a large amount of light to intermediate-light hydrocarbons, and is suitable for CO_2-EOR. The purity of CO_2 (Tianyuan Co., Ltd., China) used in this work, is 99.99 mol%. Core samples with almost the same permeabilities and porosities, collected from the same tight oil reservoir, are used in the experiments (see Table 2). More detailed data about cores that can prove their homogeneity and isotropy are given in the Appendix A2. Due to their similar properties, the effect of different core samples on the diffusion coefficient can be negligible.

Table 1
Compositional analysis results of cleaned dead oil.

Carbon number	mol%	Carbon number	mol%	Carbon number	mol%
C_1	0.00	C_8	0.54	C_{15}	8.30
C_2	0.00	C_9	0.79	C_{16}	6.32
C_3	0.00	C_{10}	2.86	C_{17}	6.17
C_4	0.00	C_{11}	9.18	C_{18}	5.18
C_5	0.00	C_{12}	11.46	C_{19}	4.62
C_6	0.00	C_{13}	12.91	C_{20+}	21.29
C_7	0.00	C_{14}	10.38	Total	100.00

2.2. Apparatus

A diffusion apparatus, schematically shown in Fig. 1, is used for the experiments. A diffusion cell, with inner diameter of 4.23 cm and depth of 11.00 cm, is used as a holder for the cores and CO_2. For all the experiments, the cores are placed vertically in the center of the diffusion cell. The CO_2 in the container is supplied from a CO_2 cylinder, whose pressure can be controlled by a high-pressure booster pump. Three kinds of pressure transducer (model DG1300-BZ-B-2-10, Senex, USA; model DG1300-BZ-B-2-20, Senex, USA; model P51, SSI, USA;), with full scale pressure of 10.0 MPa, 20 Mpa, 40.0 MPa and full scale accuracy of 0.25%, 0.25%, 0.5%, respectively, are used to measure the pressure in the diffusion cell. All experiments are conducted with the most proper pressure transducer to make sure the accuracy of the data. A water bath (model HH-SB, Jinnan Co., Ltd., China), of accuracy 0.1 °C, is used to control the temperatures of the CO_2 container and diffusion cell (dotted area in Fig. 1).

2.3. Experimental procedure

The procedure for measuring the CO_2 diffusion coefficients in the tight formation cores is briefly described as follows:

(1) The core samples, collected from the tight oil reservoir, are cleaned and dried. Then, they are placed in a container, and evacuated for more than 10.0 h before they are saturated with crude oil.
(2) The crude oil is pumped into the container under ambient temperature until the pressure reaches 15.0 MPa. It is laid aside for 48.0 h for oil saturating. Their pore volumes are determined by using weight difference and oil density, while their permeabilities are determined with nitrogen gas flooding, by using the Darcy equation before oil saturation. The measured permeabilities and porosities range from $0.058 \times 10^{-3}\,\mu m^2$ to $0.192 \times 10^{-3}\,\mu m^2$ and