Experimental Measurement of CO₂ Diffusion Coefficient in Porous Media using NMR Micro-Imaging

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Abstract. In the recent years, using CO₂ injection into oil reservoirs to enhanced oil recovery (CO₂-EOR) has attracted more and more attention from industry and laboratory experiment. The mass transfer and diffusion of CO₂ in oil is one of the key parameters of displacement process. In this study, by employing nuclear magnetic resonance (NMR) and a nonlinear fitting equation, the effective diffusion coefficient is calculated quantitatively. It proved that the experimental apparatus and mathematical procedure employed in this study were reliable to investigate and calculate the diffusion coefficient. Three main conclusions were obtained from this study: (i) the effective diffusion coefficient increases as the initial pressure increases; (ii) the relationship between CO₂ diffusion coefficient and pressure is nonlinear; (iii) the temperature effect on diffusion of CO₂ in oil is obvious because of the reduction in oil viscosity.

Introduction

CO₂ injection into oil reservoirs to enhance oil recovery has been widely practiced in the oil industry. It can both enhance the oil recovery and realize CO₂ geological sequestration. The efficiency of CO₂-EOR(CO₂ enhanced oil recovery) greatly depends on the dissolution of CO₂ in oil and the property of oil after CO₂ dissolving into. Molecular diffusion is an essential mechanism controlling the performance of CO₂ injected into oil recovery[1]. The role of molecular diffusion is to help CO₂ dissolve in the crude oil, reduce the effect of viscous fingering, decelerate gas breakthrough, and finally increase the oil production rate[2]. Consequently, the study of CO₂ diffusion process and measurement of diffusion coefficient are essential for CO₂ injection operations and reservoir simulation[3].

Recently, non-intrusive detection methods such as X-ray computer-assisted tomography (CAT) and magnetic resonance imaging (MRI) have been extended to the area of diffusion research. Nuclear magnetic resonance (NMR) offers benefits for measuring coefficients of self-diffusion, when microscopic information of porous media can be obtained. The NMR pulsed field gradient (PFG) method is non-invasive which is necessary for the determination of diffusion coefficient[4]. Li et al.[5]obtained the apparent diffusion coefficient mapping of the oil and water in porous media using NMR. Muir et al.[6]and Marica et al.[7]realized the measurement of diffusion coefficient of H₂O diffusion in D₂O-saturated porous media combining Fick’s second law using NMR.

In previous papers, the application of MRI to obtain the diffusion coefficient was presented. But it doesn’t involve the diffusion of gas into liquid. Thus, the purpose of this study is to evaluate the feasibility of quantitative analysis of the process of CO₂ diffusion and mass transfer in oil-saturated porous media using MRI, and investigate the impact of different experimental conditions on diffusion coefficients.
Experimental measurements

A schematic diagram of the experimental setup is shown in Fig. 1. The gas cylinder is a constant-volume (500-mL) stainless steel cylinder wrapped with an electric heater. The MRI sample vessel is made of polyimide to hold the diffusion samples. The outlet was blocked in the experiments. The sample vessel is divided into two layers. The inner tube is used for carrying sample, it has high pressure resistance. The outer tube is used for providing space for circulated liquid. Inert liquid Fluorinert™ FC-40 was used to control the temperature of the sample vessel because it does not contain hydrogen atoms. The temperature of the sample in the vessel is controlled by a circulator with a temperature control range of $-45$ to $200$ °C and precision of ±0.5 °C. The carrier of oil in the sample vessel is a glass tube with 10cm height and diameter of 1cm. The gas cylinder and sample vessel formed a dual-chamber system, which can improve the stability of pressure and accuracy of measurement compared with single-chamber system.

In this study, CO$_2$ with 99.99 % was used as the gas phase, and tetradecane with 99 % purity was used as the oil phase in the experiments. Temperature of 30°C and 20°C are selected. The glass beads (BZ02) used in the experiments was made in Japan, the grain size distribution ranging from 0.177-0.250 mm. It is used to fill the glass tube as porous media.

Mathematical analysis

Diffusion coefficients were calculated from model of semi-infinite media (Crank,1956)$^8$ as followed:

$$
\frac{C_y - C_s}{C_i - C_s} = \text{erfc}(\frac{y}{2\sqrt{D_p \cdot t}})
$$

(1)

Where $C_y$ is the gas concentration at distance $y$ from the influx boundary, $C_i$ is the gas concentration at the influx boundary, $C_s$ is the initial gas concentration in the porous media, $\text{erfc}$ is the error function, $D_p$ is the overall diffusion coefficient, and $t$ is time.

The images obtained by NMR reflect the information of oil-phase concentration, because of the diffusion of gas, the signal intensity of oil-phase declines and the range of change is low. In consideration of the fluctuation of diffusion coefficient calculated by each position and each time, at the distance $y$, oil concentration of early time $t_1$ subtracts oil concentration of latter time $t_2$ using equation (1), the following formula can be gotten:

$$
C_y(t_1) - C_y(t_2) = K \cdot \left( \text{erfc}(\frac{y}{2\sqrt{D_p \cdot t_1}}) - \text{erfc}(\frac{y}{2\sqrt{D_p \cdot t_2}}) \right)
$$

(2)

Where $K$ is the constant.

Nonlinear fitting the concentration difference data in two different time and each position $y$ data using equation (2), the diffusion coefficient $D_p$ of gas into oil is used as an adjustable parameter to obtain the best match of these data. Then the diffusion coefficient can be obtained.
Because equation (2) is deduced by the assumption of semi-infinite media, this method can only be used in situations that CO₂ has not reached the bottom of the oil phase. The situation is general in practice application of CO₂-EOR. The advantage of equation (2) is the influence of concentration change near the interface can be ignored, and the constant effect is removed by subtraction in the differential-profile approach.

Results and discussions

$t_1$ was set to 24 min. Considering the time of CO₂ diffuse into the bottom of porous media saturated by tetradecane was about 192 min, $t_2$ was set to 48 min, 96 min, 144 min, 192 min. The fitting result of CO₂ into porous media saturated tetradecane in 4 Mpa of 192 min is shown in Fig. 2.

As we can see from Fig. 2, each curve initially showed this increase trend because of the diffusion of CO₂. With the restriction of diffusion depth, a decrease trend appeared later in the curve.

The best match diffusion coefficient can be obtained by fitting data of four different time in one condition using equation (2). Averaging the four diffusion coefficient, the value of effective diffusion coefficient can be gotten. Fig. 3 is the summary of measurements of CO₂ diffusion coefficient in tetradecane at different initial pressure and temperature.

As shown in Fig. 3, with range of test temperature and pressure, the effective diffusion coefficient increased as the initial pressure increased. The effective diffusion coefficient of CO₂ in oil was in the range of $0.91 \times 10^{-9}$ to $1.75 \times 10^{-9}$ m²/s at 30°C, the effective diffusion coefficient of CO₂ in oil was in the range of $0.47 \times 10^{-9}$ to $1.09 \times 10^{-9}$ m²/s at 20°C. And at the low pressure, growth of effective
diffusion coefficient was small, while at the high pressure, growth was high, so the relationship between effective diffusion coefficient and pressure is not a linear relationship can be obtained. As for the effect of temperature, the effect on diffusion of CO$_2$ in oil is obvious. The effective diffusion coefficient increased as the temperature increased. The reason for this phenomenon is thermal motion of molecules increase because of the increase of temperature, the diffusion phenomenon exacerbates, besides, due to the increase of temperature, the viscosity of oil decrease, it is good for the diffusion of CO$_2$ in oil.

Conclusion

In this study, a non-invasive MRI method for measuring the diffusion coefficient of CO$_2$ into oil saturated porous media sample has been presented, a nonlinear fitting equation for calculating effective diffusion coefficient has been presented and used. The advantage of this equation is the influence of the concentration change near interface can be ignored. They are reliable to investigate and calculate the effective diffusion coefficient of carbon dioxide in oil. The following conclusions can be drawn from this study:

1. With range of test temperature and pressure, the effective diffusion coefficient increases as the initial pressure increases.
2. The relationship between CO$_2$ diffusion coefficient and pressure is nonlinear.
3. The temperature effect on diffusion of CO$_2$ in oil is obvious because of the reduction of oil viscosity.

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