Experimental Measurement of CO_2 Diffusion Coefficient in Porous Media using NMR Micro-Imaging

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Abstract. In the recent years, using CO_2 injection into oil reservoirs to enhanced oil recovery (CO_2-EOR) has attracted more and more attention from industry and laboratory experiment. The mass transfer and diffusion of CO_2 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 CO_2 diffusion coefficient and pressure is nonlinear;(iii) the temperature effect on diffusion of CO_2 in oil is obvious because of the reduction in oil viscosity.

Introduction

CO_2 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 CO_2 geological sequestration. The efficiency of CO_2-EOR(CO_2 enhanced oil recovery) greatly depends on the dissolution of CO_2 in oil and the property of oil after CO_2 dissolving into. Molecular diffusion is an essential mechanism controlling the performance of CO_2 injected into oil recovery[1]. The role of molecular diffusion is to help CO_2 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 CO_2 diffusion process and measurement of diffusion coefficient are essential for CO_2 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 H_2O diffusion in D_2O-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 CO_2 diffusion and mass transfer in oil-saturated porous media using MRI, and investigate the impact of different experimental conditions on diffusion coefficients.

Experimental measurements

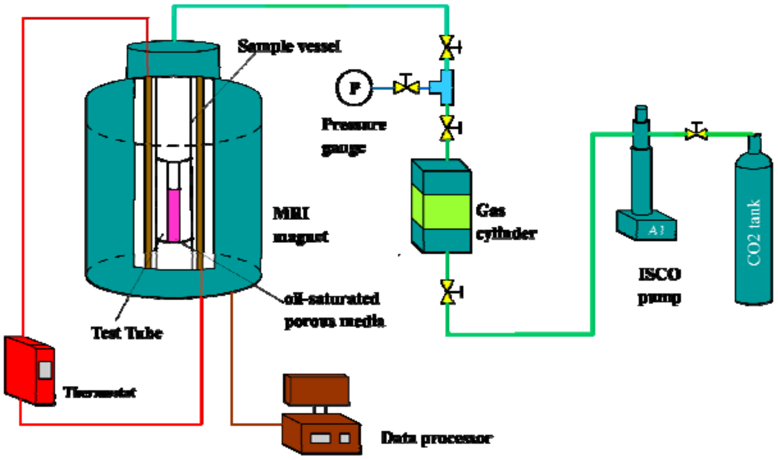

Fig. 1 Schematic of the experimental apparent for the diffusion coefficient measurement

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:

$$\frac{C_y - C_0}{C_1 - C_0} = erfc\left(\frac{y}{2\sqrt{D_p \cdot t}}\right) \tag{1}$$

Where C_y is the gas concentration at distance y from the influx boundary, C_0 is the gas concentration at the influx boundary, C_1 is the initial gas concentration in the porous media, *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:

$$C_y(\mathrm{t}_1) - C_y(\mathrm{t}_2) = \mathrm{K}\cdot(\mathrm{erfc}(\frac{y}{2\sqrt{D_p \cdot t_2}}) - \mathrm{erfc}(\frac{y}{2\sqrt{D_p \cdot t_1}})) \tag{2}$$

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 situation that CO_2 has not reached bottom of oil-phase. The situation is general in practice application of CO_2-EOR. The advantage of equation (2) is the influence of the concentration change near interface can be ignored, and the constant effect is removed by subtraction in the differential-profile approach.

Results and discussions

t_1 was set 24min. Considering the time of CO_2 diffuse into the bottom of porous media saturated by tetradecane was about 192min, t_2 was set to 48min, 96min, 144min, 192min. The fitting result of CO_2 into porous media saturated tetradecane in 4Mpa of 192min is shown in Fig. 2.

As we can see from Fig. 2, each curve initially showed this increase trend because of the diffusion of CO_2. 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 CO_2 diffusion coefficient in tetradecane at different initial pressure and temperature.

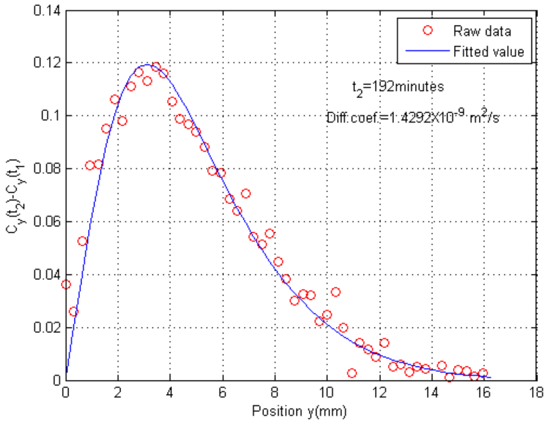

Fig. 2 Diffusion process of CO_2 into porous media saturated Tetradecane in 4Mpa of 192min

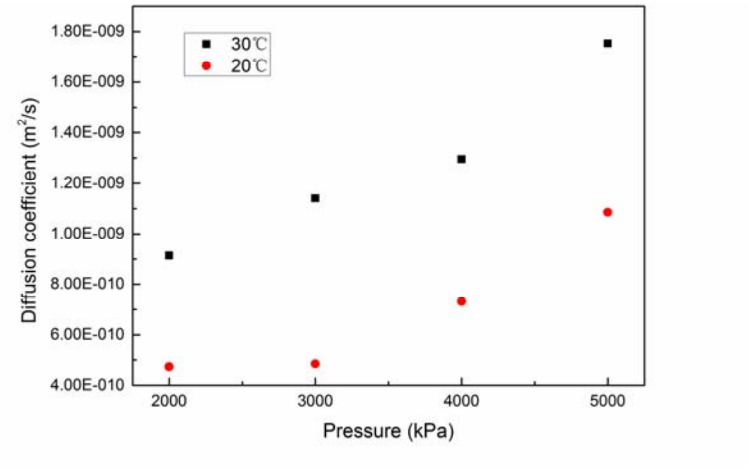

Fig. 3 Comparison of CO_2 diffusion coefficient at different initial pressure and temperature

As shown in Fig. 3, with range of test temperature and pressure, the effective diffusion coefficient increased as the initial pressure increasde. The effective diffusion coefficient of CO_2 in oil was in the range of 0.91×10^{-9} to 1.75×10^{-9} m^2/s at 30℃, the effective diffusion coefficient of CO_2 in oil was in the range of 0.47×10^{-9} to 1.09×10^{-9} m^2/s at 20℃. 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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