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The effect of permeability on supercritical CO_2 diffusion coefficient and determination of diffusive tortuosity of porous media under reservoir conditions

Songyan Li[a,*], Chenyu Qiao[a], Zhaomin Li[a], Yuting Hui[b]

[a] College of Petroleum Engineering, China University of Petroleum (East China), Qingdao, Shandong, 266580, People's Republic of China
[b] First Oil Production Plant, Daqing Oilfield, 163000, People's Republic of China

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ABSTRACT

A general method for determining the diffusivity coefficient of supercritical CO_2 in cores saturated with oil is presented in this paper. Theoretically, a mathematical model including Fick's diffusion equation and Peng–Robinson Equation of State (PR EOS) is proposed to evaluate the mass transfer of CO_2 in the cores with different permeabilities. Experimentally, the pressure-decay method is employed by monitoring the CO_2 pressure in the diffusion cell during diffusion experiments. The CO_2 diffusion coefficients in the cores with different permeabilities are determined when the discrepancy of the calculated and measured pressure-decay curves has been minimized. The diffusion coefficient of supercritical CO_2 increases gradually with rising permeability at the range of 0.1–10 mD, and then it reaches a plateau at the permeability range of 10–300 mD. The impact of the permeability on the CO_2 diffusion coefficient is attributed to the pore radius and pore structure of the cores. The Pore radius of the core whose permeability is less than 10 mD is less than 1 μm, and pore walls restrict CO_2 mass transfer under such condition, which accounts for the relative low diffusion coefficient. When the permeability exceeds 10 mD, the pore radius is larger than 1 μm, and the influence of the solid boundary is negligible. Moreover, the textural coefficients of cores decrease with the permeability, which shows that the less tortuous pore structure facilitates the mass transfer process. Diffusive tortuosities for the cores with different permeabilities are determined by using the CO_2 diffusion coefficients in porous media and bulk phase, which show the same trend with the pore radius distribution.

1. Introduction

As the worldwide increasing concern on environment protection and controlling carbon emission, techniques like Carbon Capture, Utilization and Storage (CCUS) emerge as the time required and become one of the hottest topics in engineering field [1–3]. Due to the interactions between CO_2 and crude oil, such as oil swelling effect [4–7], oil viscosity reduction [8–10] and light-hydrocarbon extraction [4,5,11,12], CO_2 can modify the properties of crude oil and enhance oil recovery (EOR) efficiently [13–16]. In addition, CO_2 EOR can also store the greenhouse gas into formations, which solves the environmental problem as well as improves the oil production. The potential storage amount of CO_2 in oil reservoirs is at least 320 billion tons based on the recent study [17]. According to its obvious advantages, CO_2 EOR methods are used in oil fields worldwide, especially in low permeable or tight reservoirs, where the water flooding is inefficient or even impossible to conduct [18–20].

CO_2 EOR methods comprise two main types: CO_2 flooding and CO_2 huff-and-puff. Moreover, molecular diffusion is the fundamental and significant process that exists in both above methods. CO_2 molecules transfer into the oil phase and modify properties of the crude oil, which is the basic mechanism for enhancing oil recovery [8,11,21,22]. The rate of gas mass transfer is defined as diffusion coefficient, which is an important parameter in reservoir numerical simulation and phase equilibrium calculation [16,18,23]. Scholars have studied the diffusion coefficient using different methods. Wen et al. [24] measured gas diffusion coefficient in asphalt with low field nuclear magnetic resonance (LF-NMR) technology, by monitoring the spectrum of the asphalt during diffusion process. They also measured the diffusion coefficient with X-ray Computer-Assisted Tomography (CAT) method [25], which obtained similar results as the NMR method does. Tick et al. [26] determined the gas diffusion coefficient in formations saturated with oil

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[*] Corresponding author.
E-mail address: lsyupc@163.com (S. Li).

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Nomenclature

A_0, B_0	empirical coefficients defined in Eq. (A6)
a_i, b_i, e_i, f_i	coefficients defined in Eqs. (A3) and (A5)
C_N	carbon number of a hydrocarbon component
c	molar concentration in bulk liquid phase, mol/m^3
c_a	molar concentration in porous media, mol/m^3
c_0	saturation molar concentration, mol/m^3
$\bar{c}$	dimensionless molar concentration
D	diffusion coefficient in porous media, m^2/s
D_b	diffusion coefficient in bulk phase, m^2/s
E_{re}	error defined in Eq. (12)
f	oil swelling factor
k	permeability of porous media, μm^2
L	geometric length of porous media
MW	molar mass, kg/mol
m_1, m_2	empirical coefficients in Eq. (9)
nc	the number of components
P	pressure, Pa
P_c	critical pressure, Pa
PN	data number of pressure-time curve
R	universal gas constant, 8.314 J/mol/K
$\bar{R}$	weighted average radius of pores, μm
	distance to the core center, m
$\bar{r}$	dimensionless radius
r_0	radius of the core, m
SG	specific gravity
T	absolute temperature, K
T_{bR}	boiling point, °R
T_{cR}	critical temperature, °R
T_r	relative temperature
t	diffusion time, s
t_{Ei}, t_{Ci}	experimental and computational times, respectively
u	expansion velocity of oil in the core, m/s
$\bar{u}$	dimensionless velocity
V	molar volume, m^3/mol
V_c	critical molar volume, m^3/mol
w	weighting parameter defined in Eq. (A8)
z_N	mole fraction of a component

Greek symbols

α	coefficient in Peng–Robinson equation of state
δ_{ij}	binary interaction parameter between components i and j
Φ	influence weight of SCN fractions
ϕ	porosity of porous media
φ	textural coefficient
λ	coefficient defined in Eq. (2)
$\langle\lambda\rangle$	real length in pores
θ	certain parameter of SCN component
Γ	tortuosity of porous media
τ	dimensionless time
ω	acentric factor

and brine, by using the sampling analysis method. These methods directly test the gas concentration distribution in liquid phase, and calculate the diffusion coefficient with Fick's diffusion equation. Such methods are known as direct measurement method. Hill et al. [27] determined CH_4 diffusion coefficient in isopentane, by using a Pressure-Volume-Temperature (PVT) cell under constant pressure. Tharanivasan et al. [21] tested CO_2 diffusion coefficient in heavy oil under different boundary conditions with pressure-decay method. Yang et al. [28] tested the CO_2 mass transfer process in crude oil by using dynamic pendant drop volume analysis technology. These methods are regarded as indirect measurement method, monitoring parameters of the liquid phase or PVT system, such as pressure, volume and swelling factor. The parameters change as the increasing concentration of gas in the liquid phase during the diffusion process. Then gas concentration distribution is determined with the correlation between the tested parameters and the dissolved gas concentration, and diffusion coefficient is finally calculated by Fick's law. Both of the two kinds of methods are feasible, while each has its own advantages. The direct methods can obtain the concentration profile directly and precisely, while these methods must rely on high precision instruments. The indirect ways can determine diffusion coefficients with simple experiments, while these ways need complex mathematical treatments.

The gas diffusion process can be classified in two fundamental categories, due to the distribution pattern of diffusion media. The first kind is gas diffusion in bulk liquid phase, such as water and oil. This diffusion process is relatively simple, which can be described with the basic mathematical model [29–32]. The analytical solution of the mathematical model can be obtained easily. This process is seldom influenced by solid boundaries, and is easy to be simulated with the PVT test. Most of available data of diffusion coefficients for CO_2 – crude oil system in literatures belong to this kind of diffusion process [1,7,16,28,29,33–35]. The other category occurs in porous media saturated with liquids, which is a more complex process. The irregular pore structure of porous media restricts the molecular movement, and the flow of swelled liquid aroused by gas dissolution is non-negligible in porous media. It makes the diffusion process more sophisticated [36,37]. Furthermore, both environmental factors like pressure and temperature, and the parameters of the porous media, such as permeability, pore size and tortuosity, influence the diffusion process obviously [38,39]. CO_2 diffusion coefficient under reservoir conditions is an important input parameter for reservoir simulation of CO_2 storage and CO_2 EOR. However, the reliable data of diffusion coefficient of supercritical CO_2 in porous media under reservoir conditions are scarce, and the influence of parameters of porous media on diffusion process is still vague.

In this study, a general method has been proposed to determine CO_2 diffusion coefficients under supercritical state in the oil-saturated cores with different permeabilities at given pressure and temperature. Theoretically, a mathematical model has been established to describe the CO_2 diffusion in cores saturated with crude oil at reservoir conditions, which consists of Fick's diffusion equation and PR EOS [40]. Experimentally, the pressure-decay method is used [36,37], by monitoring and recording the pressure in diffusion cell during experiments. There are several advantages for choosing this method. First, the pressure-decay measurement is relatively simple, which can be conducted at oilfield conveniently without depending on costly instruments. Second, the method can simulate reservoir conditions (high pressure and elevated temperature) easily, which makes the test result reflect the true situation under such conditions. Third, compared with the direct methods, the pressure-decay method is more accurate for the diffusion in porous media under reservoir conditions. Common direct methods like sampling are not feasible for diffusion in porous media, because sampling process must introduce obvious error to the result due to the change of pressure and temperature before and after sampling. While the pressure-decay method can determine diffusion coefficients without interrupting experiments. The CO_2 diffusion coefficients in the cores with different permeabilities are determined when the discrepancy between the calculated and measured pressure-decay curves are minimized. In addition, tortuosity of the cores is determined, and the effect of the permeability of cores on diffusion coefficient is analyzed.