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Enhanced oil recovery mechanism of CO_2 water-alternating-gas injection in silica nanochannel

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HIGHLIGHTS

- Molecular dynamics simulation was firstly used to address CO_2 WAG in nanochannel.
- The different roles of $scCO_2$ slug and water slug in CO_2 WAG injection were revealed.
- The synergistic effects of $scCO_2$ slug and water slug were proposed.

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ABSTRACT

CO_2 water-alternating-gas (WAG) injection has been proven as a promising and effective technology to significantly enhance the recovery of the residual oil. However, the detailed displacing process and exquisite interaction mechanism still remain ambiguous. By using Nonequilibrium Molecular Dynamic Simulation (NEMD), three comparative displacement processes of adsorbed oil layer in nanoslit using water, supercritical carbon dioxide ($scCO_2$), and CO_2 WAG injection were conducted to study the enhanced oil recovery (EOR) mechanism of CO_2 WAG injection. Simulation results indicate that the $scCO_2$ and water play different roles in CO_2 WAG: the $scCO_2$ slug could selectively dissolve apolar oil components, and the water slug provides stable water/$scCO_2$ promoting interface, which compels the miscible oil/$scCO_2$ slug out of the nanoslit. Furthermore, the synergistic effects of $scCO_2$ slug and water slug were found to account for a decreased injecting pressure and an improved dissolution capability of $scCO_2$ slug, which endows the CO_2 WAG higher oil recovery efficiency than that of both $scCO_2$ injection and water injection. Our work here provides a comprehensive interpretation of EOR mechanism of CO_2 WAG, and the results could provide insights into the optimization of the engineering process.

1. Introduction

Enhancing oil recovery (EOR) is an unremitting pursuit in the petroleum field. After an initial quick extraction, most of the residual oil stays inside the reservoir on adsorption status [1,2]. In order to displace the residual oil, numerous oil-displacing agents have been developed [2–5], such as the surfactant, the polymer, nanoparticles, and the $scCO_2$. Among them, $scCO_2$ exhibits great advantages due to its unique properties, such as its large diffusion rate approximately equal to gas, and high dissolving capability similar to liquid [6,7]. $ScCO_2$-EOR has been confirmed to be a success technique to reduce the residual oil saturation [5,8].

However, due to the extremely low viscosity, the displacement front of $scCO_2$ is inherently unstable and viscous fingering often happens and causes an early breakthrough, resulting in low volumetric sweep efficiency [2,9]. To disentangle this problem, CO_2 WAG technique was developed. Experimental researches demonstrated that, in CO_2 WAG injection, the water slug could improve the volumetric sweep efficiency, and the $scCO_2$ slug could enhance the oil displacement ratio [10–12]. In current opinions, the CO_2 could diffuse into and swell the crude oil to reduce its viscosity [13]; meanwhile, the CO_2 also distributes at the interface between oil and water to reduce the interfacial tension [14,15], which favor forming of their miscible phase. In addition, the water dissolved with CO_2 could corrode and broaden the channel. These advantages will facilitate improving the EOR. However, limited to the detecting method to observe the displacing process of crude oil in opaque and nanoscale channel, the underlying mechanism of microscopic interaction mechanism and the synergistic effect between the $scCO_2$ and the water slug is not very clear. Therefore, the in-depth understanding the microscopic mechanism of the WAG is

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fundamentally significant for improving EOR. Whereas, due to the nano- and micro-scale size of the porous reservoirs, conventional fluid theory (such as Darcy's law) is no longer suitable in such small scale [16]. Further, because of the invisibility of rock reservoirs and the great difficulty in preparing the synthetic core with a comparable porous structure to the real core, it is still a formidable challenge to obtain the detailed information of the displacing process.

In the past decades, molecular dynamics (MD) simulation has been fully developed and exhibits great advantages offering dynamic atomic-level information. In addition, some studies have been conducted to investigate the influence of the residual water [16], surface wettability [17], polarity of oil components [18], and various additives [4,17] on the oil displacement. And, the behavior of the $scCO_2$-substituted nanopore oil has drawn dramatically increasing research interest [19–21]. These studies shed light on the oil displacement behavior in water injection and $scCO_2$ injection. However, to the best of our knowledge, there exist very limited studies on the CO_2 WAG injection in nanopore [22,23]. The detailed displacing process and microscopic interaction is still unclear.

In this work, under the employment of NEMD simulations, three parallel displacing processes using $scCO_2$, water and CO_2 WAG injections were investigated. The roles of $scCO_2$ and water slugs in the CO_2 WAG injection were analyzed, and some synergistic effects of $scCO_2$ slug and water slug were found to be responsible for high oil recovery efficiency. Our work provides an atomic-level understanding of the CO_2 WAG process, and the results would be useful to realize some engineering phenomena in CO_2 WAG and guide the application of $scCO_2$ in the tertiary oil recovery efficiency.

2. Experimental and simulation

2.1. Nanoscale slit

The initial silica lattice was derived from the database of the Material Studio software, and a α-quartz silica supercell with orthorhombic dimensions (xyz) of $24.6 \times 81.1 \times 97.6$ Å^3 was constructed, the detailed building process could be seen in Supporting information (SI). Considering there are abundant nanoscale pores in the size range of 30–80 Å in rock reservoir [24], a nanoslit with a height of 63 Å along y-axis was built through deleting the middle part of silica supercell, and the exposed surface was (0 0 1). The silica surface was hydroxylated by hydroxyl with a density of 9.6 nm^{-2}, which is consistent with the result of crystal chemistry calculations (5.9–18.8 nm^{-2}) [25].

2.2. Adsorbed oil layer

Here, decane and asphaltene were selected as representative apolar and polar components of crude oil. The molecular configurations of decane and asphaltene are displayed in Fig. 1a and b, respectively. A detailed explanation for the selection of these two oil components could be found in SI. To obtain equivalent adsorbed oil layer, 10 asphaltene and 40 decane molecules was spread evenly onto the silica surface with dimensions (xz) of 24.6×68.0 Å^2, and an energy minimization and a subsequent 1 ns MD simulation were performed [27]. In order to conveniently observe the displacement consequence, these two adsorbed oil layers were placed onto the left side of the nanoslit. In the adsorbed oil layer, due to the strong interaction between the polar asphaltene and the hydroxylated surface, asphaltene molecules could preferentially adsorbed onto the surface, meanwhile the decane molecules adsorb onto the unoccupied silica surface and wrap the adsorbed asphaltene molecules [26–29], as presented in Fig. 1d–f.

2.3. Fluid

Based on the typical reservoir condition, a temperature of 330 K and pressure of 20 MPa were selected in our simulation, and the corresponding density of $scCO_2$ (0.743 g/cm^3) and water (0.993 g/cm^3) were adopted in the initial model, according to *National Institute of Standards and Technology's (NIST) database (2011)* [30]. By adding certain number of CO_2 and water molecules into box, the pressure (20 MPa) at 330 K could be maintained. The amount of added CO_2 and water molecules could be calculated from the Peng–Robinson equation according to their density [31], and is listed in Table S1 in SI. As shown in Fig. 1d ($scCO_2$) and e (water), a fluid box with dimensions (xyz) of $24.6 \times 81.1 \times 130.0$ Å^3 was set on the left side of silica nanoslit which was also filled with the fluid. As to the CO_2 WAG model (Fig. 1f), it is composed of a water slug (left) and a $scCO_2$ slug (middle) with same length of 65 Å, and the nanoslit filled with water. In these three models, a silica sheet was placed on the left of the fluid as slab to push the fluid across the channel.

2.4. MD simulation

The NEMD simulation was performed with LAMMPS package [32] through employing EPM2 CO_2 model [33] and a simple point charge (SPC) water [34]. The CLAYFF force field [35] and CHARMM force field [36,37] were used for silica and oil molecules, respectively. Detailed parameters could be found in Table S2 in SI.

The MD simulations were conducted in NVT (the number of molecules, volume and temperature are constant) ensemble at 330 K with the Nosé–Hoover thermostat [38]. During simulation, the leftmost silica sheet was defined as a rigid body and a constant velocity 1 m/s along z axis was applied to it to push the fluid across the channel; and the two silica slabs of nanoslit were kept frozen except for the modified hydroxyl. The periodic boundary condition was applied in all directions. The particle-particle particle-mesh (PPPM) algorithm [39] with a convergence parameter of 10^{-4} was used to treat the long-range electrostatic interactions. The van der Waals interactions were calculated with a cutoff (10 Å). A time step of 1 fs was used, and the corresponding data was collected in every 5 ps. A 13 ns simulation was conducted for all three systems. The configuration snapshots were rendered by VMD software [40].

3. Results and discussion

In the WAG injection process, the $scCO_2$ slug and water slug will alternately pass through the reservoir pore. Sometime the pore was filled with the $scCO_2$ slug, and in the next period, the pore will be occupied by the water slug. Hence, the displacement behaviors in the single $scCO_2$ injection and single water injection were analyzed firstly to unveil their roles in the displacement process. And then, a detailed CO_2 WAG injection process was studied to unveil the EOR mechanism of the CO_2 WAG.

3.1. The displacement behavior of $scCO_2$ and water

3.1.1. Displacement phenomena

Fig. 2 presents several sequential snapshots in the $scCO_2$ injection. As shown, nearly all decane molecules dissolve into the $scCO_2$ phase, and asphaltene molecules could only slip on but cannot detach from the silica surface. Detailed observation manifests that