Evaluation of the Driving Effect of the CO_2 Viscosity Enhancer Composite System in Extra-Low Permeability Sandstone Reservoirs

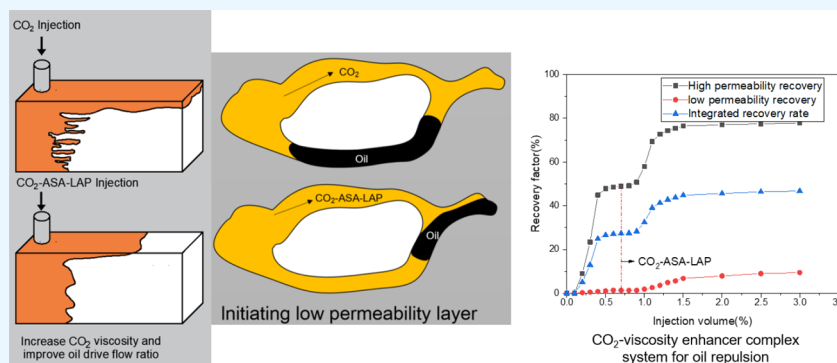Yuanwu Dong,* Hao Hu, Rui Wang, Siyao Wang, Wenyu Meng, Zequn Chen, and Shanfa Tang

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CO2-viscosity enhancer complex system for oil repulsion

ABSTRACT: CO_2 flooding is an important technology to enhance oil recovery and realize effective storage of CO_2 in ultra-low permeability reservoir. However, due to poor reservoir properties, strong interlayer heterogeneity, and unfavorable mobility ratio of CO_2, gas channeling easily occurs, resulting in low recovery. Chemically assisted CO_2 thickening technology has been developed to control the gas flow rate and improve the CO_2 repulsion effect. Through solubility and viscosity enhancement tests, the CO_2 viscosity enhancer composite system is preferably constructed and then combined with the core drive experiments, the effect of CO_2 viscosity enhancer composite system on oil drive in homogeneous and non-homogeneous cores is evaluated, the correlation between the drive efficiency and viscosity enhancement and solubility of the system is analyzed, and the mechanism of recovery enhancement is explored. The results show that the preferably constructed CO_2−ASA-LAP composite system has a good effect for improving the gas drive effect under simulated formation conditions, and its improvement effect is positively related to the solubility and viscosity increase of the system. Combining oil repelling efficiency and economic considerations, ASA:LAP = 1:1 is selected as the optimal CO_2 viscosity enhancer composite oil repelling system. For homogeneous cores, the CO_2−ASA-LAP combined system drive can increase the recovery rate by 6.65% as compared with CO_2 flooding. For heterogeneous cores, when the permeability difference is 5, the comprehensive recovery factor of the CO_2−ASA-LAP system flooding is 8.14% higher than that of CO_2 flooding. When the permeability difference increases from 5 to 10, the comprehensive recovery factor of the CO_2−ASA-LAP system flooding increases by 1.85%.The injection of the CO_2−ASA-LAP system has some injurious effect on the permeability of the reservoir core, and the smaller the permeability, the greater the degree of injury. The mechanism of the CO_2−ASA-LAP system to improve recovery includes increasing CO_2 viscosity, improving the oil repelling flow ratio, blocking high seepage channels, initiating low seepage residual oil, enhancing CO_2 dissolution, and expanding the oil repelling effect.

1. INTRODUCTION

Currently, with the recovery of international oil prices and the gradual implementation of carbon peaking and carbon neutral targets, CO_2 gas drive enhanced oil recovery technology, which can achieve both effective CO_2 storage and enhanced recovery of oil and gas reservoirs, is highly favored.[1−5] Supercritical CO_2 in the oil and gas system has special physical and chemical properties. First, its density is close to liquid, viscosity is close to gas, and has strong solvation ability and high diffusion coefficient. Second, because of its good mass transfer performance, supercritical CO_2 is also an ideal medium for reservoir energy supplement. The oil displacement mechanism

of supercritical CO_2 flooding mainly includes: reducing crude oil viscosity, reducing interfacial tension, solubilizing swelling, miscible effect, molecular diffusion, dissolved gas flooding, acidification, and so forth. Many oil and gas reservoirs at

domestic and abroad have achieved good social and economic effects through the application of CO_2 flooding,[6−9] which also shows that CO_2 flooding has great application prospects.

Based on the distribution of remaining oil and gas resources and the adaptability of CO_2 injection drive technology, it is important to focus on grasping the development of low permeability and extra-low permeability reservoirs. CO_2 injection drive can solve the problem that conventional repellents are difficult to effectively inject into low permeability and extra-low permeability reservoirs. However, due to the low viscosity and low density of the gas, the gas drive is strongly influenced by the non-homogeneity of the reservoir, and the gas injection process is often faced with poor control of gas fluidity and problems such as viscous finger entry, gravitational overburden, the gas scramble, and so forth. High flowability of gas will reduce sweep efficiency and adversely affect enhanced oil recovery.[10,11] In addition to the sealing technology, the existing methods to improve the recovery of CO_2 flooding are mostly focused on reducing the minimum miscible pressure to implement miscible flooding, increasing the viscosity of the displacement phase CO_2 to adjust the mobility and sweep ability.[12−14] Related studies show that[15] it is more important to increase the macroscopic sweep volume of the CO_2 flooding than to reduce the minimum mixing pressure during the CO_2 injection drive. Given that fluid density is mainly influenced by the formation environment (temperature and pressure), CO_2 fluidity control techniques are mostly studied in the direction of increasing the viscosity of the injected fluid, such as water−air alternation,[16] depth migration-controlled CO_2 foam,[17] supercritical CO_2 microemulsion,[18] direct CO_2 viscosity enhancement,[19] and so forth. The most direct way to reduce CO_2 fluidity is to add one or more chemical agents to CO_2 to thicken the viscosity. By controlling the viscosity of CO_2, a reasonable flow ratio can be ensured. At present, the CO_2 viscosity enhancers researched at domestic and abroad mainly focus on fluorination, chain hydrocarbons, and silanes.[20] Kilic et al.[21] prepared a series of aromatic acrylate-fluoroacrylate copolymers as CO_2 thickeners by controlling the ratio of monomer content, in which the copolymers with 71 mol % of fluoroacrylate had better solubility in CO_2 and achieved the best thickening effect, and the viscosity could be further improved with increasing pressure. Tapriyal[22] prepared benzoyl-vinyl acetate copolymer (polyBOVA) by grafting benzoyl chloride onto polyvinyl acetate-vinyl alcohol [P(Vac-co-VA)] based on the better pro-CO_2 property of vinyl acetate, catalyzed by 4-dimethylpyridine and was able to increase the viscosity of CO_2 at 298 K, polyBOVA mass concentration of 1 and 2, respectively, were able to increase the viscosity of CO_2 by 1.4 and 1.8 times, while the cloud point pressure of polyBOVA-CO_2 solution reached 64 MPa when the mass concentration was 3 wt %, and the dissolution conditions were more severe. O'Brien et al.[23] synthesized a series of aromatic amide-functionalized low molecular weight polydimethylsiloxane (PDMS) and evaluated their solubility and thickening ability in supercritical CO_2. The results showed that anthraquinone-2-carboxamide-containing end-group PDMS derivatives could thicken supercritical CO_2 with the aid of hexane solubility, with the best thickening effect using anthraquinone-2-carboxamide-capped PDMS13, which was able to increase the viscosity of CO_2 by a factor of 9 at 20.7 MPa, 298.15 K, and CO_2 thickener dosage of 13.3 wt %. Although fluorine-containing CO_2 viscosity enhancers show significantly better solubility and viscosity enhancement in

CO_2 than chain hydrocarbons and siloxanes due to their low cohesion energy and pro-CO_2 characteristics, they are mostly at the laboratory research stage due to their poor economic effect and biological toxicity; the solubility of chain hydrocarbon CO_2 viscosity enhancers in CO_2 is limited by the molecular weight, and low molecular weight compounds have good solubility in CO_2, and the viscosity enhancement effect is mediocre; long-chain high viscosity enhancers have good solubility in CO_2 or the viscosity enhancement effect is mediocre. The long-chain polymeric hydrocarbon CO_2 viscosity enhancers are similar to most siloxane-based CO_2 viscosity enhancers, which have poor solubility in CO_2 and need to add a lot of additives to promote dissolution, resulting in a high cost of thickening CO_2 and potential damage to the reservoir.[24,25]

For such problems, an environmentally friendly surfactant-based CO_2 viscosity enhancer ASA was used in the indoor experiments. This viscosity enhancer can significantly improve the solubility in CO_2 with the assistance of additives and can significantly increase the CO_2 viscosity. In order to provide new ideas and theoretical references for the design of CO_2 oil repelling scheme in extra-low permeability sandstone reservoirs, we conducted core repelling experiments and core damage evaluation experiments to investigate the "synergy" between CO_2 and viscosifier composite system in oil repelling process in extra-low permeability sandstone reservoirs and the influence of the repelling method on the actual oil repelling efficiency.

2. RESULTS AND DISCUSSION

2.1. Dissolution and Viscosity Building Properties of Viscosity Enhancers in Supercritical CO_2. The solubility and viscosity of different viscosity enhancers in supercritical CO_2 under reservoir conditions (50 °C, 8.9 MPa) are shown in Table 1. It can be seen that different viscosifiers and

Table 1. Solubility and Viscosity Data of Viscosity Enhancers and Viscosity Building Aids in CO_2 (50 °C, 8.9 MPa)

type	solubility (g/L)	viscosity (mPa·s)
PDMS (700)	39.44	0.84
PDMS (1000)	19.87	0.55
PDMS (1500)	12.48	0.38
PDMS (3200)	8.01	0.27
PDMS (5000)	3.05	0.24
adhesion enhancer ASA	1.46	0.21
viscosity increasing additives LAP	0.52	0.35
ASA + LAP(1:1)	40.9	2.16
PDMS (700) + LAP (1:1)	22.46	0.86

viscosifying additives have certain solubility and viscosifying property in supercritical CO_2, among which the solubility and viscosifying property of PDMS decreases with the increase of molecular weight, the solubility and viscosifying effect of viscosifying agent ASA, and viscosifying additives.

LAP is not good when used singly. However, compounding PDMS with LAP did not improve the effect. In general, the solubility and viscosity enhancement test methods in the experimental section can effectively evaluate the solubility and viscosity enhancement performance of different types of viscosity enhancers.

2.2. Tackifying Performance of the Tackifier-Additive Compound System in Supercritical CO_2. In order to further investigate the synergistic thickening law between the tackifier ASA and the tackifier LAP, the solubility and viscosity of the tackifier ASA/tackifier LAP compound system in supercritical CO_2 at different ratios were studied under reservoir conditions (50 °C, 8.9 MPa) (the experimental results are shown in Figure 1).With the increase of the
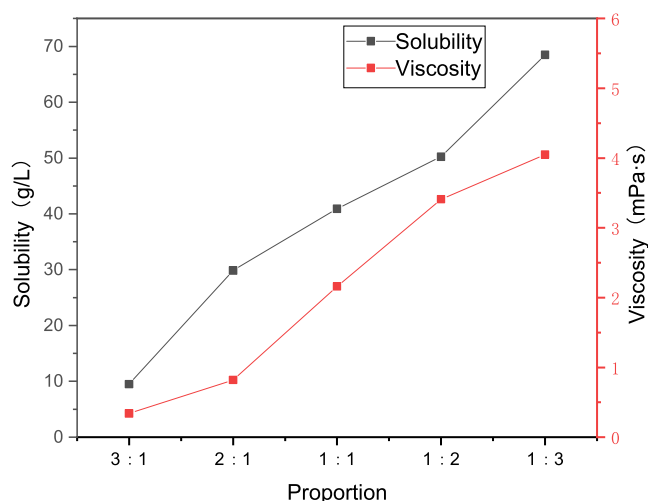

Figure 1. Solubility and viscosity of the tackifier ASA tackifier LAP compound system in supercritical CO2 at different ratios.

proportion of tackifying additives, the solubility of the compound system increased significantly, and the tackifying effect was also significantly enhanced. When the proportion of tackifying additives increased from 25 to 75%, the viscosity of the system increased from 0.34 to 4.05 mPa·s. It shows that there is a good synergistic effect between the tackifier ASA and the tackifier LAP. The proportion of additives plays a leading role in the synergistic effect, and the low proportion of additives cannot effectively play the role of tackifying. Therefore, it is necessary to further combine the actual needs of the target reservoir, by adjusting the proportion of additives to optimize the CO_2 thickening system.

2.3. Homogeneous Core Oil Drive Effect. The construction of the ASA-LAP composite system is a key factor affecting the oil drive effect and economic efficiency. The oil drive efficiency curves of CO_2 and CO_2−ASA-LAP composite system are shown in Figure 2, and detailed data are shown in Table 2 after the water drive of single pipe outcrop cores in the same permeability range (kg = 5 mD) at 50 °C.

The water drive starts with a long water-free oil recovery phase, and water drive is followed by a continuous CO_2 flooding and CO_2−ASA-LAP composite system drive, and the drive efficiency all shows a trend of slow rise and rapid rise stabilization. The introduction of viscosity-enhancing system ASA-LAP can improve the CO_2 flooding effect to a certain extent, and its improvement effect is positively related to the solubility and viscosity-enhancing property of the system, the higher the solubility and the stronger the viscosity-enhancing property, the better the effect of improving the recovery rate, and the phenomenon of foam oil flow can be observed in the export section during the drive replacement. The reason for this phenomenon is that the supercritical CO_2 in contact with the crude oil phase will effectively start the residual oil in the
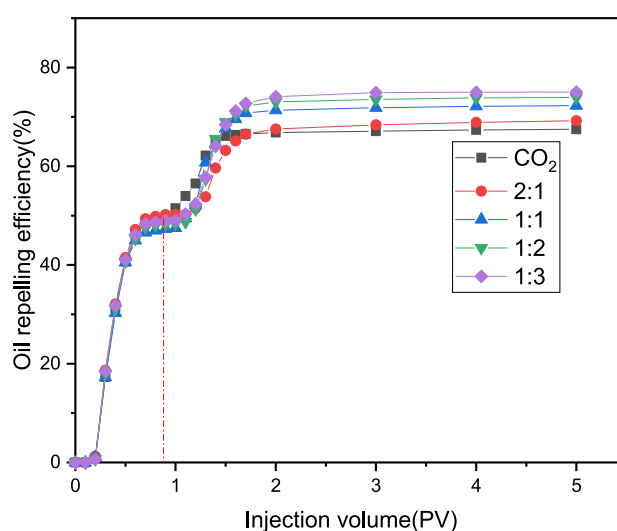

Figure 2. Curve of displacement efficiency and injected PV number of CO_2−ASA-LAP composite system in the homogeneous core.

pore channel that has not been reached by water repulsion by reducing the interfacial tension, solubilizing and swelling, and dissolving the gas repulsion, so the oil repulsion efficiency can be increased rapidly while continuing to increase the injection volume, CO_2 occurs viscous finger in through the core until the phenomenon of gas scramble occurs, and this seepage process can only carry a small amount of residual oil, so the subsequent CO_2−ASA-LAP composite system can improve the flow efficiency of high-fluid CO_2 through low-fluid crude oil by increasing viscosity of CO_2, and increase the utilization rate of CO_2, which can effectively delay the time of CO_2 to occur gas flushing and effectively expand the wave volume of subsequent fluids.

Although the oil drive efficiency increased with the increase in the percentage of additives, when the percentage of additives was less than 50%, the oil drive efficiency of the system showed a rapid growth trend with the increase in the percentage of additives, while after the percentage of additives was higher than 50%, the growing trend of oil drive efficiency slowed down with the increase in the percentage of additives (Figure 1). For example, when the percentage of additives increased from 33 to 50%, the recovery improvement increased by 5.92%, and when the percentage of additives increased from 50 to 75%, the recovery improvement only increased by 1.14%, so the contribution of increasing the percentage of additives to the recovery increase was small. Combined with the oil drive efficiency and economic considerations, it is suggested to choose the viscosity increasing system (ASA:LAP = 1:1) with 50% of additives as the optimal CO_2 viscosity increasing agent composite oil drive system (Figure 3).

2.4. Effect of Oil Repelling from Non-homogeneous Cores. At 50 °C, we investigated the effect of the CO_2 flooding to improve the recovery rate with water drives to 98% at a permeability grade difference of 5 between the two cores, and the effect of CO_2—viscosifier (ASA:LAP = 1:1) combined system drive to improve the recovery rate with water drive to 98% at a permeability grade difference of 5 and 10 between the two cores. The relationship between injection volume and oil drive efficiency is shown in Figure 4, and detailed data are shown in Table 3.

Table 2. Solubility and Viscosity Data of Adhesives and Adhesives in CO_2 (50 °C, 8.9 MPa)

repulsion system	permeability/mD	water-drivenrecovery rate/%	final recovery/%	improved recovery/%
CO_2	5.401	49.17	67.48	18.31
ASA:LAP(2:1)	5.54	50.18	69.22	19.04
ASA:LAP(1:1)	5.142	47.32	72.28	24.96
ASA:LAP(1:2)	5.157	48.24	73.94	25.7
ASA:LAP(1:3)	5.234	48.94	75.04	26.1
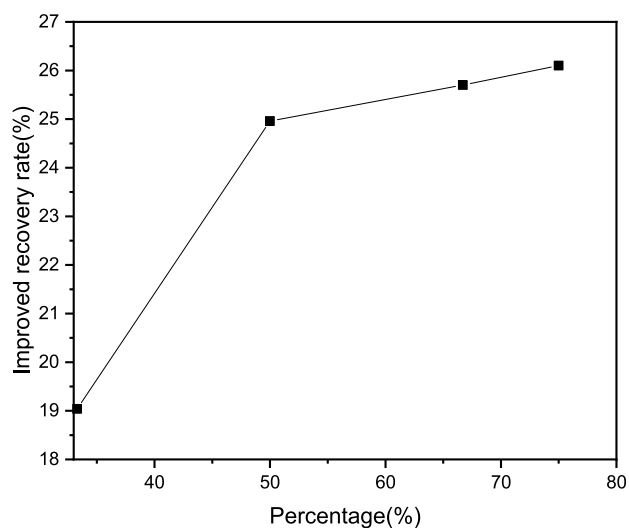
Figure 3. Relationship between the percentage of additives and oil drive efficiency.

(a) Oil drive efficiency after water drives to CO_2 at a permeability pole difference of 5

(b) The CO_2−ASA-LAP complex system oil drive efficiency after water drive to CO at an extreme permeability difference of 5

(c) Oil drive efficiency after water drive to the CO_2−ASA-LAP complex system at an extreme permeability difference of 10

The water drive recovery rate is more obviously affected by the permeability grade difference of double pipe cores; the recovery rate of high permeability pipe cores is always higher than that of low permeability pipe; the larger the permeability grade difference, the lower the recovery rate of corresponding low permeability pipe cores; and the existence of the permeability grade difference accelerates the difficulty of water drive in low permeability channels or the difficulty of using low permeability formations. At an extreme permeability difference of 5, after the water drive to 98% water content, the use of continuous CO_2 to improve the recovery rate is less effective, and the recovery rate of high permeability pipe core increases more (20.25%), but the recovery rate of low permeability pipe core is lower only 0.79% increase. It indicates that in the non-homogeneous extra-low permeability reservoir, the use of a single CO_2 flooding cannot reach the relatively low permeability area in the formation, and the comprehensive recovery improvement effect is not obvious, while the use of CO_2−ASA-LAP drive after the water drive increases the recovery rate by 8.08% in the low permeability pipe core and 29.28% in the high permeability pipe core, both of which are significantly higher than that of CO_2 flooding, indicating that the introduction of ASA-LAP does have a better effect on the non-homogeneous core or reservoir. This indicates that the introduction of ASA-LAP does have a

good effect of oil washing or improving oil drive efficiency on the non-homogeneous cores or reservoirs, which may be closely related to the mechanism of dissolution, extraction, and swelling of remaining oil in the high permeability channels by CO_2. After the permeability polar difference was increased from 5 to 10, the enhanced recovery of the low permeability pipe increased significantly from 8.08 to 16.46%, and the increase of recovery increased with the increase of permeability grade difference, which should also prove that the system can seal the relatively high permeability channel and initiate the residual oil in the low permeability channel.

2.5. Effect of the CO_2−ASA-LAP Composite System on Reservoir Rock Damage. Considering that the introduction of ASA-LAP may cause some degree of damage to the reservoir rocks, the changes of water measured permeability before and after CO_2−ASA-LAP drive for different permeability cores were investigated at 50 °C. The experimental results are shown in Table 4.

After injecting the CO_2−ASA-LAP system into the cores with different permeabilities, the permeability of water measurement will be reduced to a certain extent, and the lower the permeability of the cores, the greater the degree of damage to the permeability of the CO_2−ASA-LAP system. When the permeability of the cores increases from 1 to 10 mD, the degree of damage to the permeability of the cores decreases from 19.178 to 4.636%. This may be related to the fact that the lower the core permeability, the smaller the corresponding pore throat, the more easily the viscosity-enhancing system is adsorbed and retained in the pores and pore throat, and it is not easy to desorb or be flushed out.

In addition, during the core damage performance evaluation experiments, it can be found that the resistance coefficient increases with increasing core permeability when switching to CO_2−ASA-LAP drive after the water drive, and the residual resistance coefficient of subsequent water drive decreases with increasing core permeability (as shown in Table 5). This indicates that the sealing ability of the CO_2−ASA-LAP system to the core has permeability selectivity. In the case of an extra-low permeability reservoir or core, the higher the permeability is relatively, the larger its pore size is relatively, and the CO_2−ASA-LAP system is easier to enter the core or reservoir pore, and the shear rate is relatively low, making the CO_2−ASA-LAP system relatively higher in viscosity, easier to seal the relatively larger pore or permeability cores, and the higher the sealing strength, the better the effect.

2.6. CO_2−ASA-LAP Composite System Oil Drive Mechanism. *2.6.1. Increasing CO_2 Viscosity and Improving Oil Drive Flow Ratio.* Combining Figures 1 and 2, it can be seen that the viscosity of the CO_2 viscosity enhancer composite system can be adjusted by adjusting the proportion of additives, and when the viscosity of the CO_2 viscosity enhancer composite system is increased, the better the effect of improving water drive recovery that is, increasing the viscosity of the CO_2 viscosity enhancer composite system can effectively
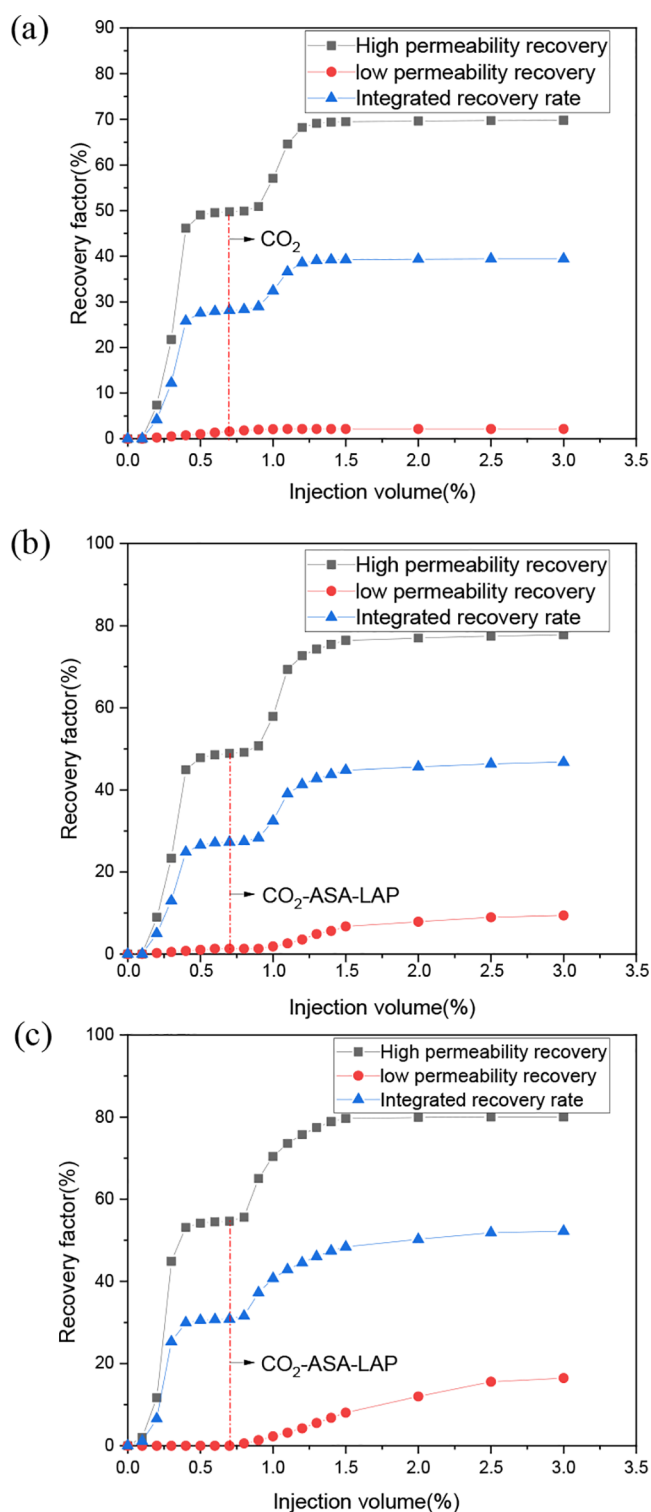
Figure 4. Relationship between oil drive efficiency and PV number of injection for CO_2 and the CO_2–ASA-LAP composite system in non-homogeneous cores.

improve the flow ratio between the replacement medium and crude oil, slow down the occurrence time of CO_2 gas migration, and improve the oil drive efficiency.

2.6.2. Blocking High Permeability Layer and Initiating Low Permeability Layer. From Tables 3 and 5, it can be seen that when the same polar difference double pipe drive, the water drive followed by the CO_2–ASA-LAP system drive increases the recovery rate of low permeability pipe 10.23 times more than that of water drive followed by CO_2 flooding. When the double pipe grade difference increases from 5 to 10, the sealing strength of CO_2–ASA-LAP to high permeability pipe is enhanced, and the recovery rate of low permeability pipe increases significantly, such as from 8.08 to 16.46%. It can be seen that the sealing ability and sealing permeability selectivity of the CO_2–ASA-LAP system to the core of the high permeability pipe makes the subsequent fluids easy to turn to divert and inject into the low permeability pipe, efficiently starting the remaining oil in the core of the low permeability pipe, and greatly improving the recovery rate of the low permeability pipe.

2.6.3. Enhancement of CO_2 Dissolution and the Swelling Oil Repellent Effect. From Table 3, it can be seen that the simple CO_2 flooding can improve the integrated recovery of the core by 11.52% on the basis of water drive through its own mechanism of solubilization and swelling of crude oil and viscosity reduction, while the CO_2–ASA-LAP system drive can further improve the integrated recovery on the basis of water drive compared with the simple CO_2 flooding. The reason for this phenomenon is that the introduction of viscosity-enhancing system ASA-LAP while increasing the CO_2 viscosity and improving the CO_2 flow rate, can further increase the CO_2 contact time with crude oil. This is because the introduction of ASA-LAP, a viscosity-enhancing system, increases the viscosity of CO_2 and improves the flow of CO_2. At the same time, it has a better blocking and shunting effect on the non-homogeneous core, which can further increase the contact time between CO_2 and crude oil, so that CO_2 can be more fully dissolved in crude oil and enhance the viscosity reduction and swelling drive of CO_2.

The mechanism of the CO_2–ASA-LAP system can be summarized as follows: increase the viscosity of CO_2, improve the flow ratio of oil drive, seal the high seepage channel, start the low seepage residual oil, and enhance the dissolution and expansion of CO_2 oil drive; among them, the viscosity increasing effect of ASA-LAP on supercritical CO_2 is the key.

3. SUMMARY AND CONCLUSIONS

(1) The viscosity enhancers ASA and viscosity enhancement additive LAP can be used in combination, which can significantly improve its solubility and viscosity enhancement effect in supercritical CO_2. The additive ratio plays a leading role in the synergistic viscosity enhancement effect, and the low additive ratio cannot effectively play the viscosity enhancement effect.

(2) Homogeneous core oil drive experiments show that the recovery of CO_2 flooding can be increased by 18.31% after water drive to 98%, and the introduction of viscosity building system ASA-LAP can improve the effect of CO_2 flooding to some extent, and its improvement effect is positively related to the solubility and viscosity building property of the system. Combined with the oil drive efficiency and economic considerations, ASA:LAP = 1:1 was selected as the optimal CO_2 viscosity enhancer composite drive system, which can improve the recovery rate by 24.96%.

(3) The oil drive experiments in non-homogeneous cores show that the CO_2–ASA-LAP system has a better effect of sealing the high permeability channel and regulating the flow rate in non-homogeneous cores or reservoirs,

Table 3. Evaluation of Oil Drive Efficiency of Non-homogeneous Cores

system	level difference	water-drivenrecovery rate/%			EOR/%		
		low osmosis	high osmosis	comprehensive	low osmosis	high osmosis	comprehensive
CO_2 flooding	5	1.35	49.52	27.91	0.79	20.25	11.52
CO_2−ASA-LAP	5	1.33	48.52	27.1	8.08	29.28	19.66
CO_2−ASA-LAP	10	0	54.51	30.73	16.46	25.5	21.51

Table 4. Degree of Permeability Injury of CO_2−ASA-LAP Drive on Cores with Different Permeabilities

gas-measured permeability/mD	water measurement permeability/mD	CO_2−ASA-LAP post-drive water measured permeability/mD	degree of penetration injury/%
1.223	0.146	0.118	19.178
4.682	0.402	0.349	13.184
11.631	0.906	0.864	4.636

Table 5. CO_2 Resistance Coefficient and Residual Resistance Coefficient of the ASA-LAP System vs Core Permeability Data

gas-measured permeability/mD	resistance factor	residual resistance coefficient
1.223	1.953	1.314
4.682	2.397	1.198
11.631	4.192	1.096

and when the polar difference is 5, the CO_2−ASA-LAP system drive increases the integrated recovery by 8.14% and the low permeability recovery by 7.29% compared with the CO_2 flooding. After the polar difference increases from 5 to 10, the CO_2−ASA-LAP system drive further improves the integrated recovery and low permeability recovery by 1.85 and 8.38%. After the polar difference was increased from 5 to 10, the integrated recovery and low permeability recovery were further improved, and the integrated recovery increased by 1.85%, and the low permeability recovery increased by 8.38%.

(4) In the injection of the CO_2−ASA-LAP system, there is some harm to the reservoir core permeability, and the degree of harm is closely related to the reservoir core permeability. Moreover, its resistance coefficient increases with the increase of core permeability, and the residual resistance coefficient of subsequent water drive decreases with the increase of core permeability.

(5) The CO_2−ASA-LAP system oil repelling mechanism includes: increasing CO_2 viscosity, improving the oil repelling flow ratio, blocking high seepage channels, starting low seepage residual oil, enhancing CO_2 dissolution, and expanding the oil repelling effect.

4. EXPERIMENTAL PART

4.1. Experimental Materials and Apparatus. The experimental water is simulated water prepared according to the ion composition and content of the actual formation water in Yanchang oilfield. The water type is $CaCl_2$ and the salinity is 79 390 mg/L. The specific ion composition is shown in Table 6. CO_2, purity 99.9%, purchased from Hunan Yuanchuang Gas Company; CO_2 surfactant tackifier ASA, provided by College of Petroleum Engineering, Yangtze University; linear block copolymer tackifier additive LAP, provided by College of Petroleum Engineering, Yangtze University; and PDMS with molecular weight of 700, 1000, 1500, 3200, and 5000, purchased from Huangshan Qiangli Chemical Co., Ltd. The core displacement experiment uses the natural outcrop core of the Yanchang oilfield in China, and the permeability is in the range of $1−10 \times 10^{-3}\mu m^2$.

The main instruments used in the experiment are shown in Table 7.

Table 7. Instruments and Factory

instrument	factory
UCP-3 high-pressure high-temperature sampler	Jiangsu Lianyou Research Instruments Co., Ltd.
LY-ND-01 kinematic viscosity tester	Jiangsu Lianyou Research Instruments Co., Ltd.
CO_2 gas multifunctional replacement physical simulation system	Haian Petroleum Research Instruments Co., Ltd.
HSB-1 high-pressure displacement pump	Haian Petroleum Research Instruments Co., Ltd.
LMF-1 wet gas flowmeter	Beijing Jinzhiye Instrument and Equipment Co., Ltd.
experimental device for core oil displacement	Changzhou Zhongbei Instrument Co., Ltd.

4.2. Experimental Methods. *4.2.1. Determination of Dissolution Performance of Viscosity Enhancers.* The solubility test device of tackifier (Figure 5) was used to record the volume change of CO_2 (pump position before and after measurement) and the mass of separated tackifier at the same pressure and temperature, so as to determine the solubility of tackifier in CO_2. Specific experimental procedure: (1) take a certain amount of tackifier samples into the middle chamber of UCP-3 high-pressure and high-temperature dispenser and seal and inject a certain pressure of CO_2; (2) connect the sample dispenser with the double-cylinder constant speed and pressure repellent pump, set the temperature and pressure required for the experiment on the control panel, then turn on
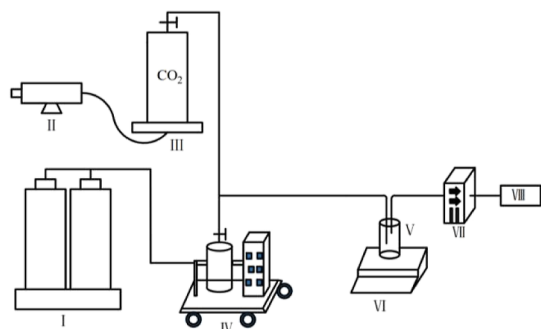
Table 6. Simulated Formation of Water Ion Composition

ion concentration (mg/L)							
Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-	mineralization degree (mg/L)
10134.4	81.29	19148.13	70.11	49233.33	653.88	98.77	79419.91

Figure 5. Diagram of solubility test of viscosity enhancer in supercritical CO_2.

the rotary inversion switch to make the CO_2 and viscosity enhancer mix well; (3) when the temperature, pressure, and pump position are basically stable, turn off the rotary inverted switch, make the sample placed in the instrument for 30 min and then record the pressure, pump position L_1; (4) connect the outlet end and gas−liquid separation device and then slowly open the valve so that the pressure is slowly reduced to the pump level of 2 mL. After closing the valve, record the quality of the liquid mass m, to be recorded after the pump level is stable at this time the pump for L_2, using Formula 1 to calculate the solubility of viscosity enhancers in supercritical CO_2; and (5) the operation was repeated three times, and the average value of solubility was obtained.

$$s = \frac{m}{L_1 - L_2} \times 1000 \tag{1}$$

4.2.2. Evaluation of the Viscosity Enhancement Effect of the CO_2 Viscosity Enhancer Composite System. The viscosity test device (Figure 6) was used to calculate the system
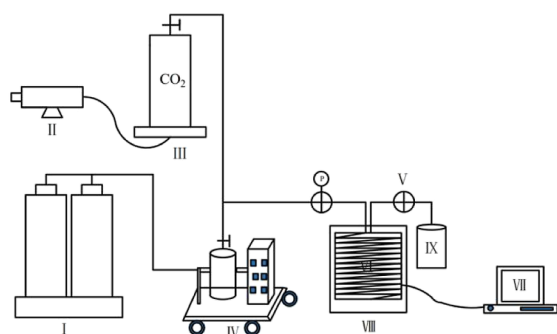

Figure 6. Schematic diagram of viscosity test of viscosity enhancer in supercritical CO_2.

viscosity by recording the relevant data of the CO_2 viscosity builder composite system at constant pump speed flowing through the capillary section of the LY-ND-01 kinematic viscosity tester ($L = 2 \times 10^3$ cm, $r = 0.05$ cm, 0.1 cm) under the set temperature and pressure, and the software was used to calculate the system viscosity, and the formula for calculating the viscosity of CO_2 viscosity builder composite system is shown in eq 2. Specific experimental procedure: (1) prepare the CO_2 viscosifier composite system under the required

temperature and pressure (same as 2.2.1); (2) when the water bath temperature of the LY-ND-01 kinematic viscosity tester reaches the experimental temperature, connect the outlet end of the middle chamber of UCP-3 high-pressure and high-temperature dispenser and set the back pressure; (3) open the valve switch at the outlet end of the intermediate chamber and set the double-cylinder constant-speed and constant-pressure repellent pump to constant-speed mode at the same time so that the CO_2 viscosity enhancer composite system enters the kinematic viscosity tester evenly; and (4) after the data is stable, close the middle chamber outlet valve, the double cylinder constant speed constant pressure displacement pump is set to constant pressure mode, to the end of the test.

$$\mu = r\frac{(p_1 - p_2)}{2L(d_v/d_r)} \tag{2}$$

r is the capillary inner diameter r_0, cm; p_1 is the inlet pressure, MPa; p_2 is the outlet pressure, MPa; d_v/d_r is the shear rate, s^{-1}; and L is the length of the capillary tube, cm.

4.2.3. Evaluation of Oil Repelling Effect of the CO_2 Viscosity Enhancer Composite System. 4.2.3.1. Homogeneous Core Flooding Experiment. Figure 7 is the process of
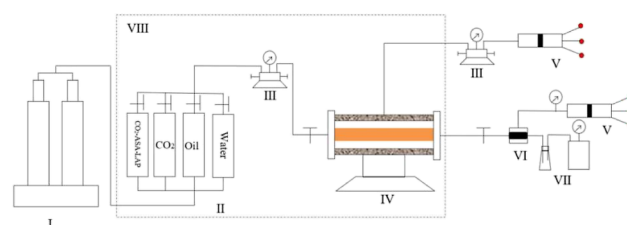

Figure 7. Homogeneous core flooding experiment process.

homogeneous core flooding experiment. Five cores with similar permeability were selected to be saturated with water, established bound water saturation and saturated oil and then aged at reservoir temperature (50 °C) for 24 h. Then, a water drive was conducted in the form of a constant-flow drive until the instantaneous water content at the outlet end of the core reached 98%, and CO_2 flooding and CO_2−ASA-LAP composite system drive experiments were conducted to compare the oil drive efficiency under different drive methods. The specific experimental procedures of saturated water, established bound water saturation and saturated oil are as follows: (1) saturated formation water: Cores with similar permeability to the experiment are weighed dry, vacuumed, and pressurized to saturate the formation water, and weighed wet after saturation, and the pore volume of the core is calculated by combining with the density of formation water; (2) established bound water saturation: At reservoir temperature, N_2 flooding is used to establish the required ideal irreducible water saturation, and the irreducible water saturation is accurately calculated by weighing the cores before and after N_2 gas flooding; (3) saturate oil: The establishment of irreducible water saturation of the core into the holder, and it is subjected to confining pressure and vacuuming. At the reservoir temperature, the reservoir pressure is established by live oil flooding, and the core pore volume (the volume of live oil entering the pump under constant pressure) is accurately measured. Then, the valve at the outlet end is opened until the
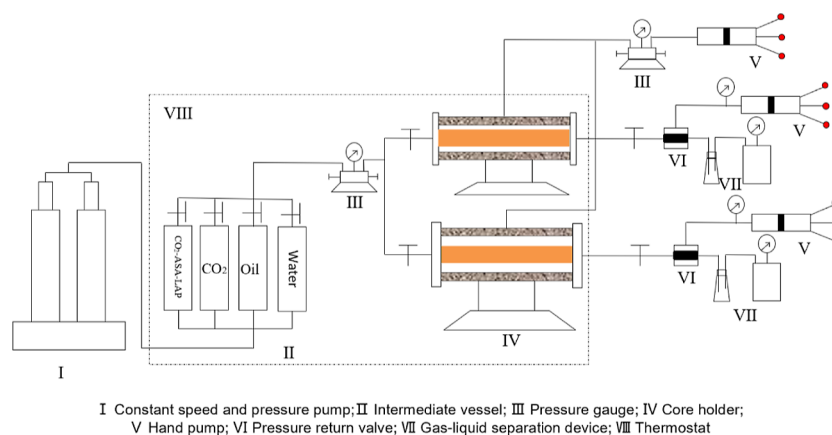
I Constant speed and pressure pump; II Intermediate vessel; III Pressure gauge; IV Core holder;
V Hand pump; VI Pressure return valve; VII Gas-liquid separation device; VIII Thermostat

Figure 8. Experimental process of heterogeneous core flooding.

gas−oil ratio of the produced oil sample at the outlet end is consistent with the compound live oil.

4.2.3.2. Non-homogeneous Material Model Oil Drive Experiment. The experimental process of heterogeneous core flooding is shown in Figure 8. The cores conforming to formation heterogeneity conditions are selected to carry out saturated water, establish irreducible water saturation and saturated oil, respectively. Then, aging for 24 h at reservoir temperature (50 °C); the core is assembled in the form of parallel connection of double-tube oil displacement. After the assembly is completed, a water flooding is carried out until the instantaneous water content at the core outlet reaches 98% and then the CO_2 flooding and CO_2−ASA-LAP composite system flooding experiments are carried out, respectively. Finally, the oil displacement efficiency under different displacement modes is compared.

4.2.4. Evaluation of Core Injury Performance. At the reservoir temperature of 50 °C, the displacement is carried out in a constant current manner. During the displacement process, the injection stable pressure difference is monitored to calculate the water permeability of the core. When the core permeability measurement is completed, the CO_2−ASA-LAP composite system is transferred to the stable pressure difference between the inlet pressure and the outlet pressure and then the constant flow water flooding is transferred. The permeability after core damage is measured, and the degree of core permeability damage is calculated. The damage rate calculation formula, resistance coefficient calculation formula, and residual resistance coefficient calculation formula of core water phase permeability are shown in Formulas 3−5, respectively.

$$\eta = \frac{K_1 - K_2}{K_1} \times 100\% \tag{3}$$

$$R_F = \frac{\Delta P_f}{\Delta P_w} \tag{4}$$

$$R_K = \frac{\Delta P_a}{\Delta P_b} \tag{5}$$

H is the injury rate, %. K_1 is the permeability before the core injury, mD. K_2 is the permeability after core injury, mD. R_F is the resistance coefficient, dimensionless. ΔP_w and ΔP_f are the pressure differences between water drive and CO_2−ASA-LAP composite system drive stabilization, respectively, MPa. R_k is

the residual drag coefficient, dimensionless. ΔP_b and ΔP_a are the water drive pressure differences before and after the CO_2−ASA-LAP composite system repulsion, respectively. MPa.

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Notes

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