applied sciences

Article

Optimization of CO_2 Injection Huff and Puff Process in Shale Reservoirs Based on NMR Technology

Yang Gao [1,2], Dehua Liu [1,2], Sichen Li [1,2], Liang Cheng [1,2] and Jing Sun [1,2,*]

[1] College of Petroleum Engineering, Yangtze University, Wuhan 430100, China; 201973009@yangtzeu.edu.cn (Y.G.); 100633@yangtzeu.edu.cn (D.L.); 202073008@yangtzeu.edu.cn (S.L.); 500636@yangtzeu.edu.cn (L.C.)
[2] Hubei Drilling and Recovery Engineering for Oil and Gas Key Laboratory, Wuhan 430100, China
* Correspondence: 500856@yangtzeu.edu.cn

Abstract: The pore mobilization characteristics of CO_2 when in shale reservoirs is an important indicator for evaluating the effectiveness of its application for enhanced recovery in shale reservoirs, and it is important to develop a comprehensive set of physical simulation methods that are consistent with actual field operations. This has underscored the need for efficient development techniques in the energy industry. The huff-n-puff seepage oil recovery method is crucial for developing tight oil reservoirs, including shale oil. However, the small pore size and low permeability of shale render conventional indoor experiments unsuitable for shale oil cores. Consequently, there is a need to establish a fully enclosed experimental method with a high detection accuracy to optimize the huff and puff process parameters. The NMR technique identifies oil and gas transport features in nanogaps, and in this study, we use low-field nuclear magnetic resonance (NMR) online displacement technology to conduct CO_2 huff and puff experiments on shale oil, covering the gas injection, well stewing, and production stages. After conducting four rounds of huff-n-puff experiments, key process parameters were optimized, including the simmering time, huff-n-puff timing, number of huff-n-puff rounds, and the amount of percolant injected. The findings reveal that as the number of huff-n-puff rounds increases, the time required for well stabilization decreases correspondingly. However, the enhancement in recovery from additional huff-n-puff rounds becomes negligible after three rounds, showing only a 1.16% improvement. CO_2 re-injection is required when the pressure falls to 70% of the initiaformation pressure to ensure efficient shale oil well development. This study also indicates that the most economically beneficial results are achieved when the injection volume of the huff-n-puff process is 0.44 pore volumes (PVs).

Keywords: shale oil; CO_2; huff and puff; on-line NMR; parameter optimization

check for updates

Citation: Gao, Y.; Liu, D.; Li, S.; Cheng, L.; Sun, J. Optimization of CO_2 Injection Huff and Puff Process in Shale Reservoirs Based on NMR Technology. *Appl. Sci.* **2024**, *14*, 2411. https://doi.org/10.3390/app14062411

Academic Editor: Nikolaos Koukouzas

Received: 7 February 2024
Revised: 10 March 2024
Accepted: 11 March 2024
Published: 13 March 2024

1. Introduction

In recent years, the issue of global climate change has become increasingly severe, making the reduction in carbon dioxide (CO_2) emissions a critical environmental challenge [1–3]. Strategies such as CO_2 geological sequestration and enhanced oil recovery have garnered significant attention for their potential to both store CO_2 underground and enhance oil extraction efficiency [4]. Shale oil, distinguished from conventional oil by its presence in free and adsorbed states within the microscopic pores of organic-rich rock formations, presents unique technical challenges [5,6]. These challenges arise from the need for advanced technologies to effectively extract and process oil from such tight formations, differentiating it from conventional oil found in larger pores and fractures.

CO_2 throughput technology has been widely used in the development of low-permeability tight sandstone oil and gas reservoirs, but its application in shale oil reservoirs is still in the stage of indoor research and field tests [7]. Shang et al. carried out experiments on the supercritical CO_2 extraction of shale oil, and investigated the effects of the injection pressure, huff and puff rounds, and core properties on the shale oil recovery rate, which increased with the increase in injection pressure; huff time has a great influence on the final recovery rate, and the longer the huff time is, the higher the recovery rate. The shale oil recovery rate increases with the increase in injection pressure. The duration of well stewing has a great influence on the final recovery rate; the longer the duration of the well stewing, the higher the recovery rate. After 36 h, the influence of the duration of well stewing on the recovery rate is weakened; the greater the number of huff and puff rounds, the higher the recovery rate [8]. Wang et al. investigated the characteristics of movable oil components in samples extracted by supercritical carbon dioxide fluids in stratigraphical temperatures and under the conditions of different fluid pressures, and the amount of oil in the samples in the different fugitive states in extraction experiments. The results show that under a certain temperature and different fluid pressures, the fluid can be used to extract the movable oil from the samples. The results show that under certain temperature and fluid pressure conditions, the carbon number of the main components of the movable oil shows a tendency to increase with the increase in the huff and puff extraction duration, and the ability of supercritical carbon dioxide huff and puff to extract movable oil increases significantly with the increase in fluid pressure [9]. Gamadi et al. carried out single-well cyclic CO_2 injection experiments by using shale oil and Eagle Ford shale samples, and adjusted the injection rate, injection pressure, and number of cycles [10]. In addition, some scholars have used numerical simulations to optimize the parameters of CO_2 huff and puff technology [11]. At present, most studies use conventional methods to accurately measure the shale oil output, and the commonly used CT technology can only be applied in qualitative research, not quantitative research [12–14]. In recent years, low-field NMR technology has been applied to shale oil reservoir core experiments on a large scale, which can not only enable the study of the microscopic transport of nanoscale pores in shale reservoirs, but also convert the relaxation time in the T2 spectrum into pore size, so as to quantitatively study the mobilization law and characteristics of crude oil in microscopic pores [15–20]. For example, Fan et al. investigated the CO_2 drive-off process at a continuous increase from 0.7 MPa to 11 MPa. The results show that from immiscible flooding to near-miscible flooding and finally to miscible flooding, the cumulative oil recovery factor exhibits a step-like growth trend under continuous multipressure point displacement, and the increase in the amplitude of the recovery rate at different displacement states decreases in turn [18].

From a comprehensive point of view, this paper combines the indoor experiments of shale oil reservoir huff and puff and the actual operation process in a mining field, selects the rock samples of a reservoir in the second section of the Gaoyou Depression in the North Jiangsu Basin, China, and conducts several rounds of fully closed indoor experiments on the CO_2 injection stage, the seepage–absorption stage of the stowed well, and the production stage of the open well by using on-line NMR technology, which simulates the real process of huff and puff oil recovery. During the experiments, the NMR T2 spectral signals were calculated to study the huff and puff characteristics and microscopic transport after the injection of the sorbent into the shale oil, optimized the parameters in the huff and puff process, and investigated the characteristics of the crude oil movement in the microscopic pores of the shale reservoir on the microscopic scale.

2. Materials and Methods

2.1. Experimental Material

Shale rock samples: The cores used in this experiment all originate from the Fu II reservoir in Gaoyou Depression, North Jiangsu Basin, China, and the mineral types are dominated by quartz, calcite, and clay minerals, with a TOC content of 0.353%, and the diameter of the samples is 25 mm and the length of the samples is 60 mm. Considering the simulation of the actual situation of the reservoirs, Brazilian splitting treatment was implemented on the samples in order to simulate hydraulic fracturing technology (Figure 1) [21]. The core base data and XRD whole rock analysis results are shown in Tables 1 and 2.

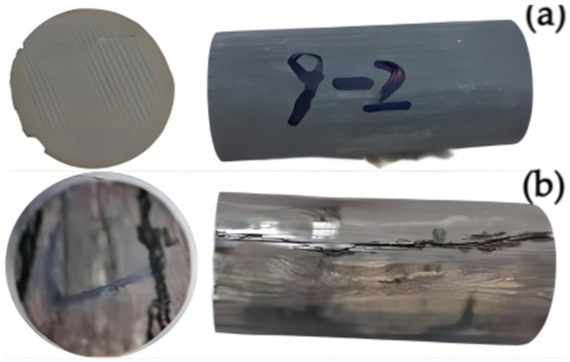

Figure 1. Core after use of the Brazilian splitting method ((**a**): shale sample 9-2, (**b**): shale sample 20-2).

Table 1. XRD whole-rock analysis results table.

Rock Sample Number	Quartz (%)	Potassium Feldspar (%)	Sodium Feldspar (%)	Anorthite (%)	Calcite (%)	Wollastonite (%)	Dolomite (%)	Pyrite (%)	Clay (%)	TOC (%)
9-2	36	2.7	12.8		4.2		1.9	42.4	36	2.7
20-2	19.4	2.3	7.5	15.3	11.6	8.7	2.6	32.6	19.4	2.3

Table 2. Basic data of experimental rock core.

Rock Sample Number	Core Volume (cm^3)	Porosity (%)	Permeability (mD)	Pore Volume (cm^3)	Saturation Condition (%)	Saturated Oil Volume (mL)
9-2	21.08	4.16	0.00175	1.208	60.27	0.728
20-2	24.62	4.32	0.01816	1.06	60.85	0.645

Experimental medium: The experimental oil is the crude oil taken from the reservoir by using the well separator. Under the original formation conditions (temperature 78 °C), its viscosity is 1.73 mPa·s. Therefore, it is necessary to reduce the viscosity of the crude oil with a viscosity of 3.82 mPa·s at the ground level to that of the formation condition by adding aviation kerosene. The experimental gas is CO_2 (99.95% purity).

2.2. Experimental Equipment and Parameters

The experimental apparatus employed was the MacroMR12-150H-I, a large-sized NMR high-temperature and high-pressure imaging analyzer, manufactured by Newmark Analytical Instruments Co., Suzhou, China (illustrated in Figure 2). This sophisticated instrument features a resonance frequency of 12.8 MHz and a magnetic strength of 0.3 Tesla. It is equipped with a replica coil measuring 25 mm in diameter, accommodating replica samples up to 25 mm in diameter. Additionally, the magnet's operational temperature is maintained at 32.5 °C.

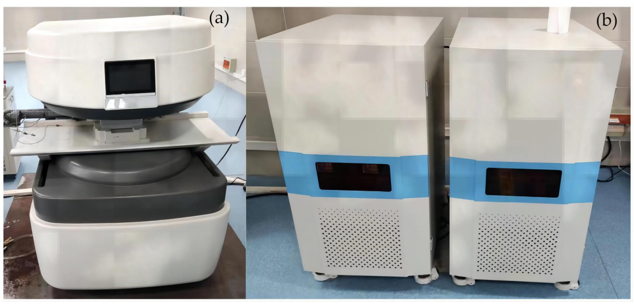

Figure 2. Nuclear magnetic resonance (NMR) ((**a**): nuclear magnetic body, (**b**): nuclear magnetic control unit).

2.3. Experimental Steps

This research aims to refine four critical process parameters in CO_2 injection for enhanced oil recovery in shale reservoirs: stewing time, huff and puff rounds, huff and puff timing, and injection volume. It is noted that the quantity of crude oil in the core diminishes with an increase in the number of huff and puff cycles, which in turn reduces the extraction efficiency across successive rounds. Consequently, optimizing the injection volume for the carrier medium requires the repeated saturation of the core. In this case, two experimental programs were designed.

Core sample No. 9-2 is utilized to perform four rounds of throughput experiments focusing on the optimal stewing time, huff and puff rounds, and huff and puff timing for these cycles.

Core sample No. 20-2 is employed to assess the impact of various injection volumes on the extraction efficiency.

2.3.1. 9-2 Shale Core Experiment Program

1. Cleaning of rock samples: High-temperature, high-pressure steam oil washing is adopted, and the solvent for oil washing is a mixed solution of benzene and alcohol. After oil washing, the samples are dried in an oven at a temperature of 90 °C until the quality no longer changes.

2. Test the basic parameters of shale (porosity, permeability, dry weight), make seams in the core, split the core in the middle, saturate the core with oil under high pressure, and measure the weight of the saturated core.

3. CO_2 is gaseous at room temperature and pressure, so it needs to be pressurized into an intermediate vessel to become liquid before injection.

4. Put the core saturated with oil (saturated with more than 60% oil) into the core gripper, add circumferential pressure and inject the percolant until the system pressure is 25 MPa, and close the injection end. The first round of well casing is more than 72 h, and the subsequent casing process will again determine the length according to the NMR data analysis.

5. The signal volume change in the core during the casing process is detected by on-line NMR until the signal volume is basically unchanged, and then the casing is stopped.

6. At the end of the simmering phase, the injection end is opened for open-well production, and production is stopped by controlling the pressure return valve so that the differential pressure is 1–5 MPa and the pressure is continuously dropped to 68% of the system pressure. During the production process, NMR data are collected after each pressure drop for production.

7. Re-inject CO_2 into the core after the first round of huff and puff, restore the system pressure to 25 MPa, and repeat steps 3–4. Four rounds of "gas injection—well stewing—extraction" were carried out in total.

8. Conclude the experiment, analyze the data, study the microscopic transport characteristics during the stewing process, and optimize the huff and puff rounds, stewing time, and injection timing.

2.3.2. 20-2 Shale Core Experimental Program

1. Saturate the core at high pressure and place the saturated core into the core gripper.

2. Inject the percolant from the entrance end, design different cumulative injection volumes to raise the system pressure to 15 MPa.

3. After CO_2 injection, simmer the well for 50 h, open the valve at the inlet end for production, and reduce the pressure to extract, huff and puff for 1 round until the system pressure drops to 70% of the original pressure, and collect NMR data.

4. Re-saturate the core to ensure that the volume difference of crude oil saturated in each time is around 0.05 g. Then, repeat the above experimental steps 1–3, so that the system pressure rises to 20 and 25 MPa, respectively.

The experimental setup included an automatic pressure tracking pump to ensure that the perimeter pressure always exceeded the system pressure by 3 MPa throughout the experiment. Figure 3 shows a schematic diagram of the experimental procedure.

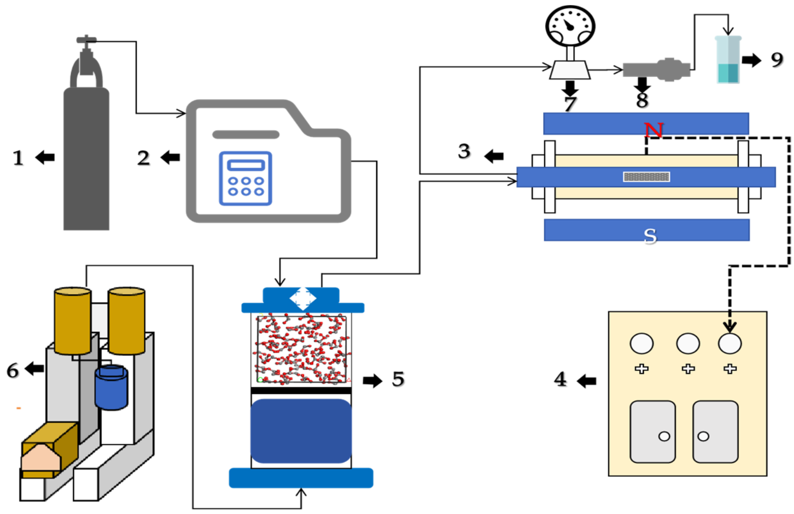

Figure 3. Schematic diagram of the flow of the experiments of segment plug injection of CO_2 huff-n-puff. 1. CO_2 gas cylinder; 2. air booster pump; 3. NMR experimental device; 4. confining pressure pump; 5. intermediate vessel (CO_2); 6. constant pressure and speed pump; 7. pressure gauge; 8. back pressure valve; 9. graduated cylinder.

3. Discussion of Experimental Results

3.1. Huff and Puff Experimental Process and Results

3.1.1. First Round of Huff and Puff Experimental Process and Results

The throughput parameters were optimized by conducting four rounds of huff and puff experiments on the experimental cores, and the content of crude oil assigned to the cores was calculated using on-line NMR equipment throughout the throughput experiments.

In the first huff and puff process, CO_2 was first injected to bring the system pressure up to 25 MPa (Figure 4a), and then the well was stewed for 65 h (Figure 4b), after which the outlet end was opened for production (Figure 4c–e). From the simmering process, it can be seen that the bimodal pattern of the NMR curve changed in signal volume, with the first peak displaying a decrease, while the second peak displaying an increase and a shift to the right. Through the conversion relationship between the relaxation time and pore size, the oil content of the different pore sizes is plotted as shown in Figure 5, from which it can be seen that the crude oil originally endowed in 0–0.02 μm is displaced into the pore sizes of 0.02–20 nm with the end of the coking process. This means that by CO_2 stewing, wells can displace crude oil from small holes into larger holes, giving it better flow paths, easier production, and improved recovery.

It can be seen from the first production process that as the system pressure decreases, the first peak of the NMR curve has a significant decrease, and the second peak has an insignificant trend of change. It can be seen from Figure 4f that the crude oil in the small hole is continuously extracted, while the oil content in the 0.02–20-micron-diameter hole displays an insignificant change and a different trend; for example, when the system pressure decreases from 23 MPa to 20 MPa, there is a tendency to increase the oil content in this hole diameter. At this stage, the system pressure decreases to 74% of the original pressure, and with the decrease in system pressure, the extraction degree of crude oil in the first round of production shale is 6.11%, as can be seen in Table 3, calculated by the signal amount of NMR.

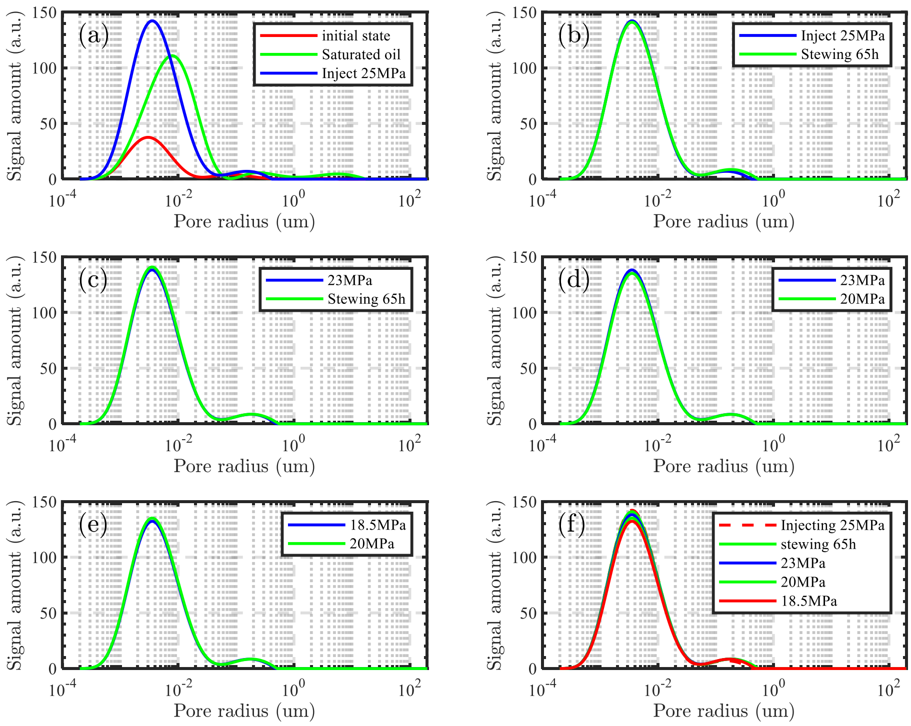

Figure 4. NMR results of the first round of huff and puff experiment. (**a**) The process of injecting CO_2 into the well (the red line is the NMR curve after drying the rock sample, the green line is the NMR curve after saturated oil, and the blue line is the NMR curve after injection of 25 MPa CO_2); (**b**) the process of stewing the well for 65 h (the green line is the NMR curve after 65 h in the well); (**c**–**e**) the changes in NMR curves under different production pressures; (**f**) the changes in NMR curves from the beginning of stewing the well to the end of the first cycle of huff and puff (23 MPa, 20 MPa, 18.5 MPa are the NMR curves corresponding to the system pressure in the production engineering).

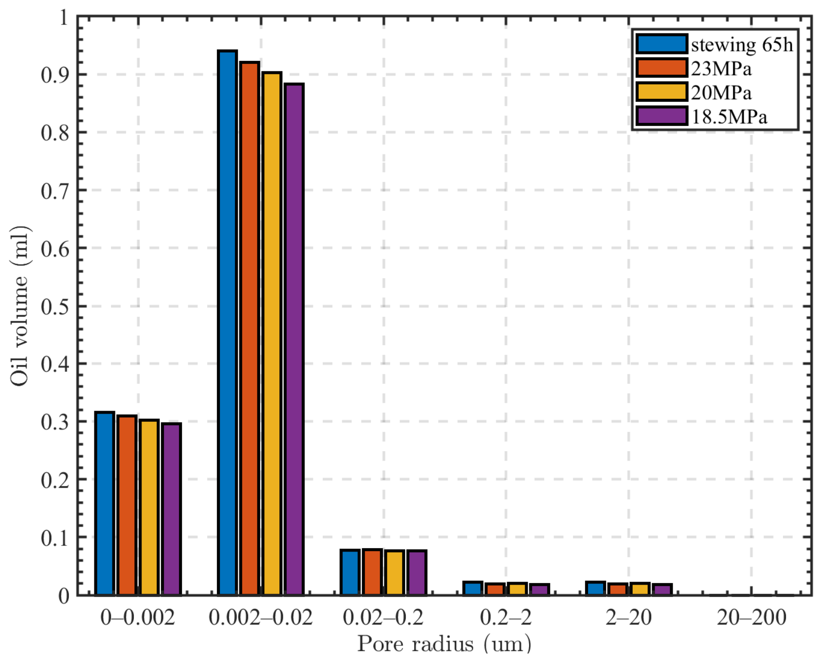

Figure 5. Variation in oil content in each pore size of the core during the first huff and puff round (the blue bar graph shows the pore size distribution after stewing the well for 65 h; 23 MPa, 20 MPa, 18.5 MPa are the pore distributions at different production pressures).

Table 3. Changes in NMR signal volume during the first huff and puff round.

Production Process	Signal	Oil Recovery (mL)	Extraction Level (%)	Cumulative Extraction Level (%)	Residual Oil Volume (mL)
The process of stewing the well for 65 h	4841.62	——	——	——	0.728
1st huff and puff-23 MPa	4743.88	0.015	2.02	2.02	0.713
1st huff and puff-20 MPa	4647.84	0.029	1.98	4.00	0.699
1st huff and puff-18.5 MPa	4545.97	0.044	2.11	6.11	0.684

3.1.2. Second Round of Huff and Puff Experimental Process and Results

After injecting CO_2 into the core at a system pressure of 25 MPa, the injection end was closed, and the process of stowing the well at a peripheral pressure of 28 MPa was carried out for 45 h. It can be seen from the second round of the production process that the two peaks of the NMR curve remain basically unchanged as the system pressure drops (Figure 6), which shows that the crude oil in the small and large holes is basically not recovered (Figure 7). At this stage, the system pressure decreased to 74% of the original pressure, and the stage extraction degree of the crude oil in the shale in the second round of production was calculated by the signal volume of NMR (Table 4) to be 3.11%, and the cumulative extraction degree was 9.22%.

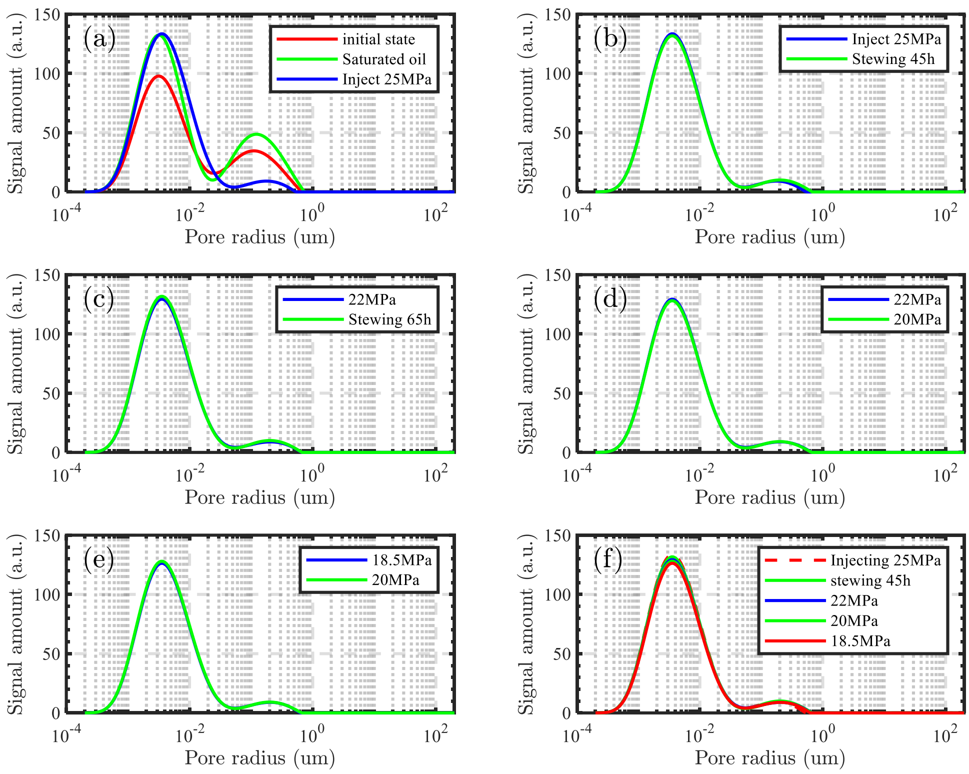

Figure 6. NMR results of the second round of huff and puff experiment. (**a**) The process of injecting CO_2 into the well (the red line is the NMR curve after drying the rock sample, the green line is the NMR curve after saturated oil is inejcted, and the blue line is the NMR curve after injection of 25 MPa CO_2); (**b**) the process of stewing the well for 45 h (the green line is the NMR curve after 45 h in the well); (**c**–**e**) the changes in NMR curves under different production pressures; (**f**) the changes in NMR curves from the beginning of stewing the well to the end of the second cycle of huff and puff (23 MPa, 20 MPa, 18.5 MPa are the NMR curves corresponding to the system pressure in the production engineering).

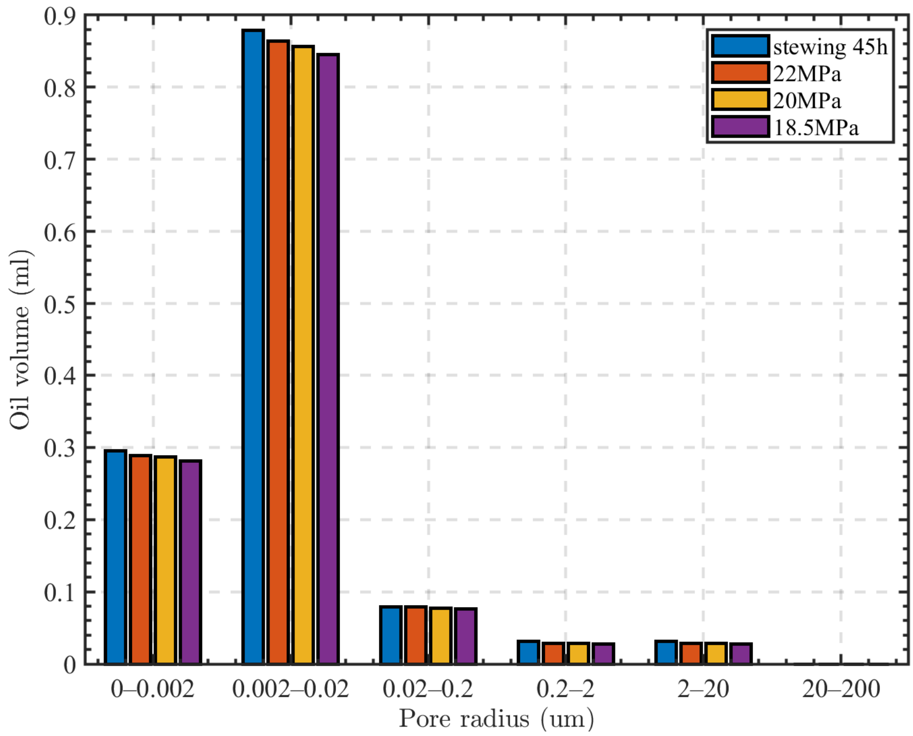

Figure 7. Variation in oil content in each pore size of the core during the second huff and puff round (the blue bar graph shows the pore size distribution after stewing the well for 45 h; 22 MPa, 20 MPa, 18.5 MPa are the pore distributions at different production pressures).

Table 4. Changes in NMR signal volume during the second huff and puff round.

Production Process	Signal	Oil Recovery (mL)	Extraction Level (%)	Cumulative Extraction Level (%)	Residual Oil Volume (mL)
The process of stewing the well for 45 h	4587.076	——	——	——	0.690
2nd huff and puff-22 MPa	4500.34	0.048	0.94	7.05	0.677
2nd huff and puff-20 MPa	4457.714	0.055	0.88	7.93	0.670
2nd huff and puff-18.5 MPa	4395.259	0.063	0.29	9.22	0.661

3.1.3. Third Round of Huff and Puff Experimental Process and Results

The stewing time during the third round of huff and puff was set to 45 h. The results of the throughput experiments are shown in Figures 8 and 9 and Table 5. In terms of the change in the oil content in the pore size, there is still crude oil in the 0.002–0.02-micrometer-pores replaced to other pores, but the change in oil quantity is basically not observed from the NMR curve. At the end of the huff and puff rounds, the stage recovery degree of crude oil was 1.16% and the recovery degree was 10.38%. With the decrease in system pressure, the two peaks of the NMR curves are basically unchanged, which represents that the crude oil in the small and large pores is basically not recovered.

Table 5. Changes in NMR signal volume during the third huff and puff round.

Production Process	Signal	Oil Recovery (mL)	Extraction Level (%)	Cumulative Extraction Level (%)	Residual Oil Volume (mL)
The process of stewing the well for 45 h	4406.645	——	——	——	0.663
3rd huff and puff-21 MPa	4386.35	0.068	0.18	9.40	0.660
3rd huff and puff-19 MPa	4353.821	0.073	0.68	10.08	0.655
3rd huff and puff-17.5 MPa	4339.02	0.076	0.30	10.38	0.652

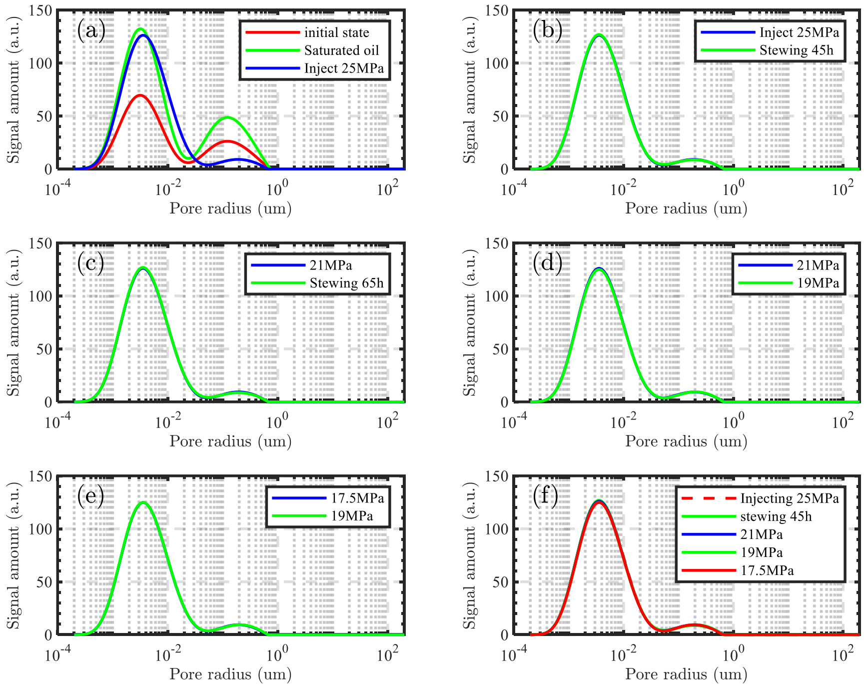

Figure 8. NMR results of the third round of huff and puff experiment. (**a**) The process of injecting CO_2 into the well (the red line is the NMR curve after drying the rock sample, the green line is the NMR curve after saturated oil is injected, and the blue line is the NMR curve after injection of 25 MPa CO_2); (**b**) the process of stewing the well for 45 h (the green line is the NMR curve after 45 h in the well); (**c**–**e**) the changes in NMR curves under different production pressures; (**f**) the changes in NMR curves from the beginning of stewing the well to the end of the third cycle of huff and puff (21 MPa, 19 MPa, 17.5 MPa are the NMR curves corresponding to the system pressure in the production engineering).

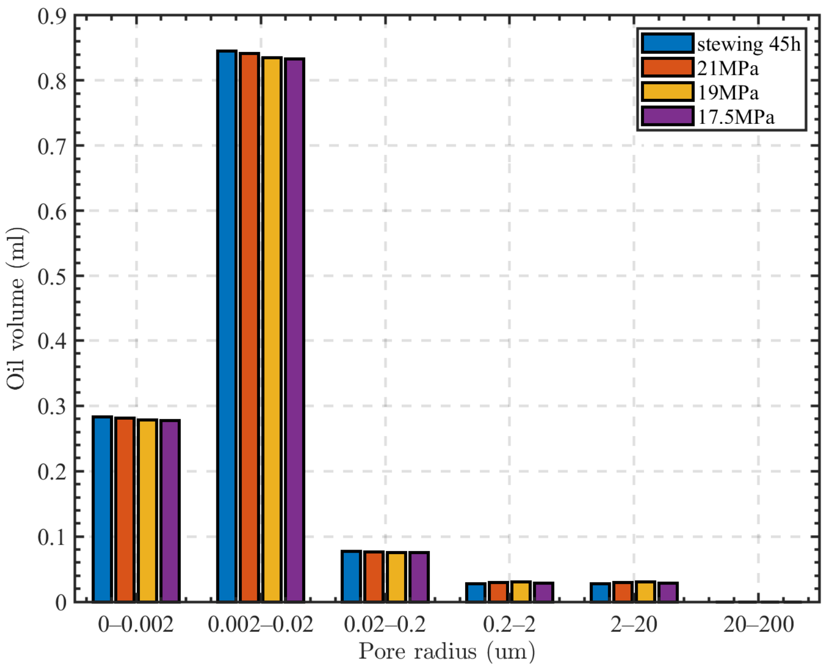

Figure 9. Variation in oil content in each pore size of the core during the third huff and puff round (the blue bar graph shows the pore size distribution after stewing the well for 45 h; 21 MPa, 19 MPa, 17.5 MPa are the pore distributions at different production pressures).

3.1.4. Fourth Round of Huff and Puff Experimental Process and Result

The stewing time during the fourth round of huff and puff was set to 50 h. From the NMR curves (Figure 10), it can be seen that, essentially, there has been no crude oil recovery, and the three curves are nearly overlapping (Figure 11), and the stage recovery of crude oil in the fourth round of production of shale is 0.46%, and the recovery degree is 10.84% (Table 6).

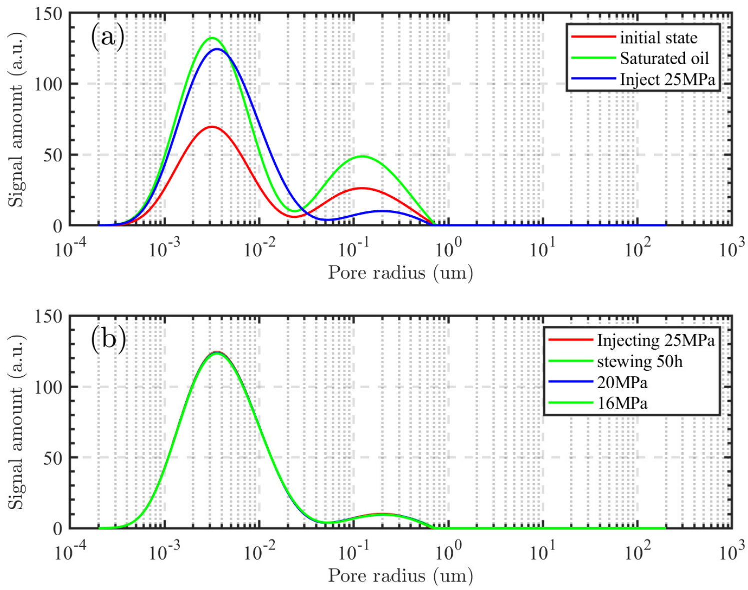

Figure 10. NMR results of the fourth round of huff and puff experiment. (**a**) The process of injecting CO_2 into the well (the red line is the NMR curve after drying the rock sample, the green line is the NMR curve after saturated oil is injected, and the blue line is the NMR curve after injection of 25 MPa CO_2); (**b**) the changes in NMR curves from the beginning of stewing the well to the end of the fourth cycle of huff and puff (the green line is the NMR curve after 45 h in the well); (20 MPa, 16 MPa are the NMR curves corresponding to the system pressure in the production engineering).

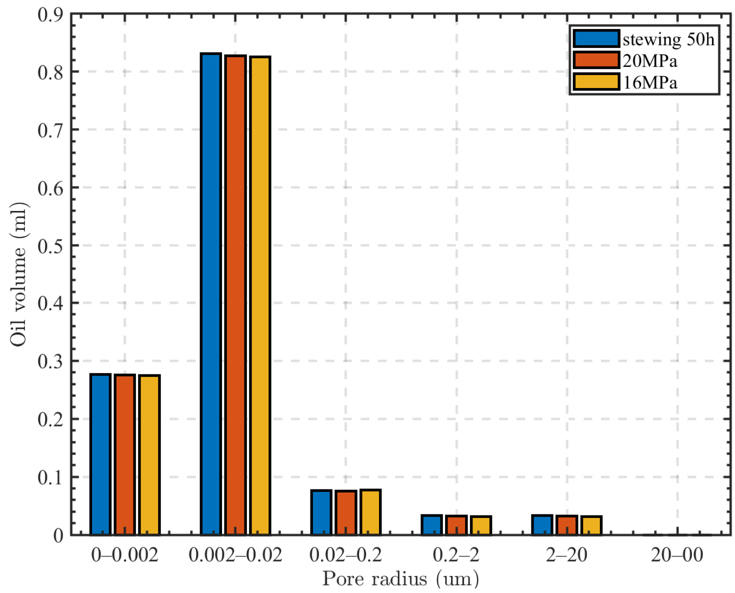

Figure 11. Variation in oil content in each pore size of the core during the fourth huff and puff round (the blue bar graph shows the pore size distribution after stewing the well for 50 h; 20 MPa, 16 MPa are the pore distributions at different production pressures).

Table 6. Changes in NMR signal volume during the fourth huff and puff round.

Production Process	Signal	Oil Recovery (mL)	Extraction Level (%)	Cumulative Extraction Level (%)	Residual Oil Volume (mL)
The process of stewing the well for 50 h	4345.707	——	——	——	0.653
4th huff and puff-20 MPa	4324.949	0.078	0.29	10.67	0.650
4th huff and puff-16 MPa	4316.79	0.079	0.17	10.84	0.649

3.2. Huff and Puff Experiments with Different Injection Volumes

The system pressure was brought to 15 MPa, 20 MPa, and 25 MPa by injecting CO_2, and the injection volume was recorded during this process. After that, a 50 h simmering well was performed and then production was carried out until the pressure dropped to 70% of the initial pressure to stop production. The injection volume was optimized by calculating the degree of crude oil recovery at the end of the three sets of experiments. The experimental results are shown in Figure 12.

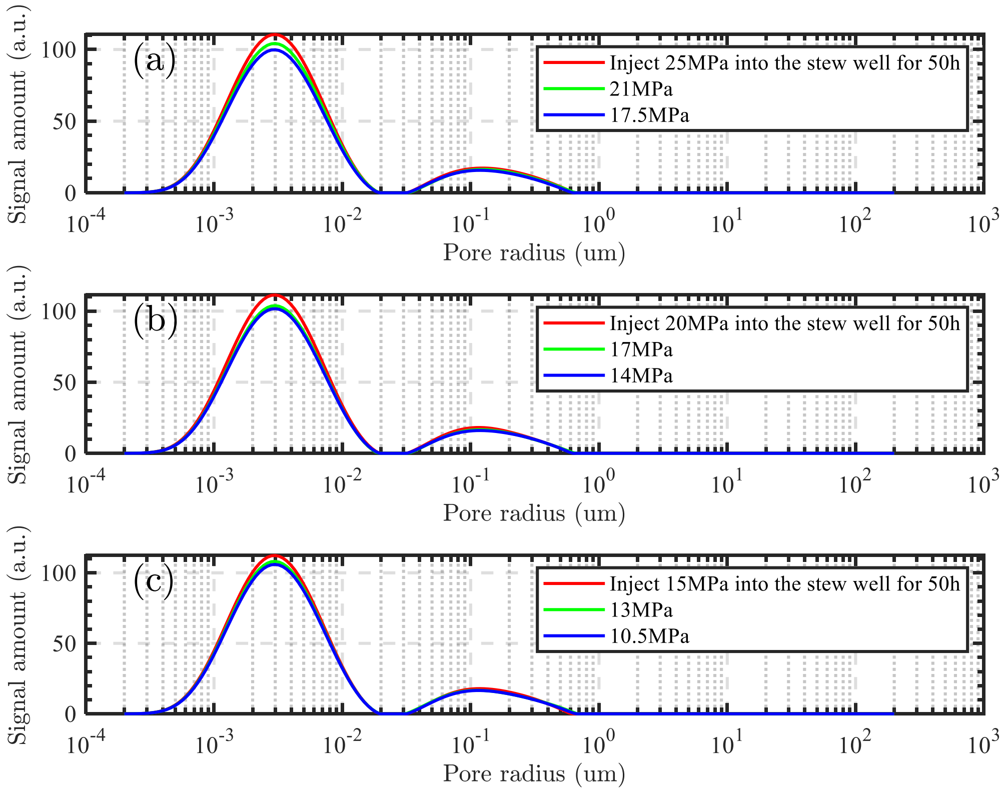

Figure 12. NMR results of experiments with different injection volumes. (**a**) NMR results of injection pressure of 25 MPa; (**b**) NMR results of injection pressure of 20 MPa; (**c**) NMR results of injection pressure of 15 MPa.

3.3. Discussion of Experimental Results

3.3.1. Optimization of Stewing Time

The stewing stage is the process of oil and gas replacement. The large hole is the main CO_2 enrichment and circulation area, in which the CO_2 can fully contact the crude oil, and then greatly increase its recovery, and the small hole has a small pore throat, and the CO_2 mainly relies on diffusion to enter the small pore space. Too short a stewing time will lead to insufficient contact between the CO_2 and crude oil, affecting the dissolved gas drive effect; too long a stewing time will lead to too far a CO_2 diffusion distance, affecting the mobilization of the crude oil near the production wells, and increasing the time cost. The changes in the signal amount of crude oil in the large and small holes during different huff and puff rounds of well cogging were collected by on-line NMR, and the results are shown in Figure 13.

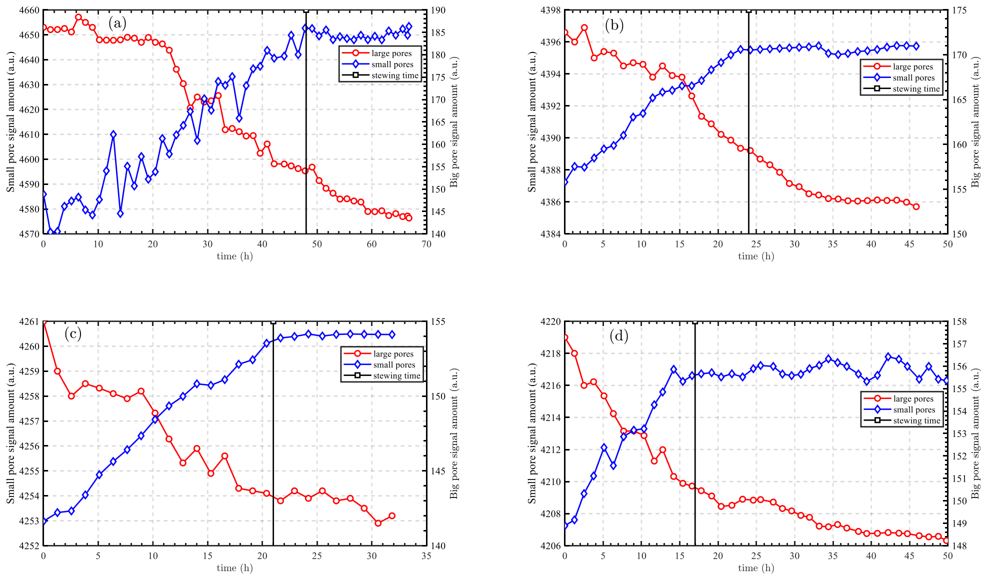

Figure 13. Crude oil changes during well casing in different rounds of huff and puff experiments. (**a**) Change in NMR signal volume for round 1 stewed wells; (**b**) change in NMR signal volume for round 2 stewed wells; (**c**) change in NMR signal volume for round 3 stewed wells; (**d**) change in NMR signal volume for round 4 stewed wells.

It can be seen that the crude oil in the small hole in the stewing process will be transported to the large hole with an increase in the stewing time, and finally reach equilibrium, and this equilibrium time point serves as the optimal time of stewing. In the four rounds of stewing, the optimal stewing time is 48, 24, 21, and 17 h. It can be seen that with the increase in the huff and puff rounds, the stewing time can be reduced appropriately.

3.3.2. Optimization of Huff and Puff Rounds

With the increase in the huff and puff rounds, the oil replacement efficiency will be reduced as well as the extraction efficiency, and the reasonable number of huff and puff rounds needs to be optimized. The changes in the NMR curves during the whole process of the huff and puff rounds and the extraction degree of different rounds are shown in Figures 14 and 15 and Table 7.

Table 7. NMR signal data for different rounds.

Huff and Puff Rounds	State	Signal	Cumulative Extraction Level (%)	Extraction Level (%)
1	Stewing well 65 h	4841.620341	0.00	6.11
	23 MPa	4743.884626	2.02	
	20 MPa	4647.844035	4.00	
	18.5 MPa	4545.979105	6.11	
2	22 MPa	4500.34	7.05	3.11
	20 MPa	4457.713783	7.93	
	18.5 MPa	4395.258746	9.22	
3	21 MPa	4386.35	9.40	1.16
	19 MPa	4353.821	10.08	
	17.5 MPa	4339.02	10.38	
4	20 MPa	4324.948887	10.67	0.46
	16 MPa	4316.79	10.84	

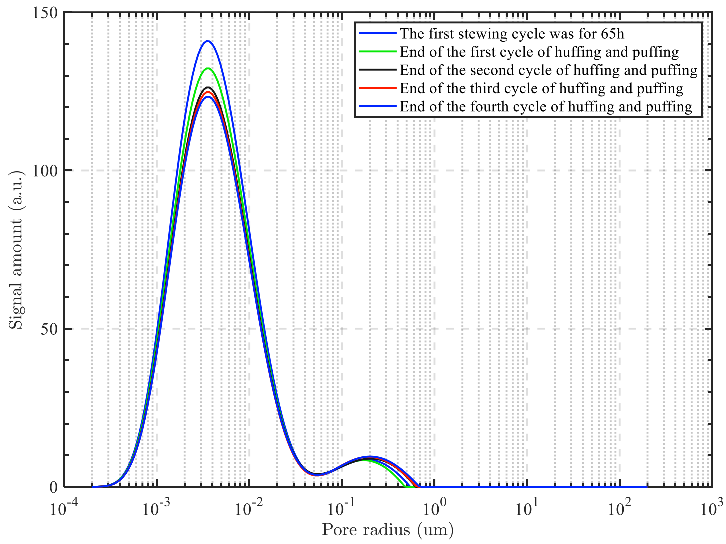

Figure 14. NMR curve changes throughout the process.

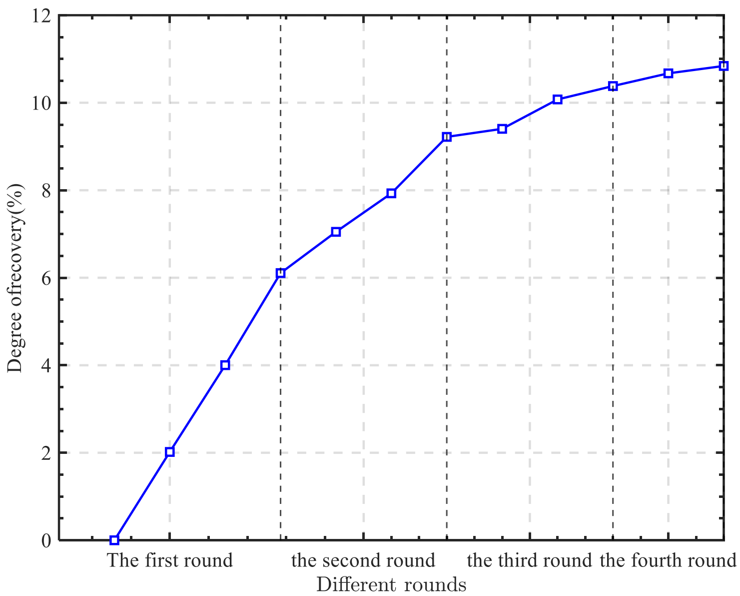

Figure 15. Degree of extraction of different rounds of huff and puff rounds (The blue line shows the extent of exploitation in different rounds).

From the analysis of the extraction degree and single-round extraction degree of the four rounds of huff and puff, it can be seen that the effect of the first three rounds of huff and puff was evident, and the single-round extraction degree was 6.11%, 3.11%, 1.16%, and 0.46%, respectively, in which the first three rounds of huff and puff phase extraction degree per round accounted for 56.4%, 28.7%, and 10.7% of the extraction degree, respectively, and the optimal recommended number of rounds of huff and puff was three.

3.3.3. Optimization of Injection Timing

In the production process, when monitoring the transportation of oil during the pressure drop process, when the pressure decreases, and when oil transportation no longer occurs, this is considered to be the best time to huff and puff. From the production results after each round of huff and puff, it can be seen that in the first two rounds of huff and puff, when the pressure drops to about 74% of the formation pressure, the oil recovery is not evident. It is recommended to inject CO_2 when the pressure drops to about 70%; if the huff and puff is continued after two rounds of huff and puff, the timing of injection needs to be advanced, and it is recommended that CO_2 be injected for the subsequent huff and puff before the formation pressure drops to 80% (Figures 4f, 6f, 8f and 10b).

3.3.4. Optimization of Injection Volume

As can be seen from Figure 12a–c, the morphology of the NMR curves changes more obviously during the production process as the injection pressure increases. According to the change in the signal amount of the NMR T2 spectra (Table 8), after simmering the well from an injection pressure of 15 MPa to 20 MPa to 25 MPa, the extraction degree changed from 5.37% to 8.69% to 9.61%, in that order, i.e., the increase in the injected amount of percolant can improve the extraction degree.

Table 8. Experimental data for injection volume optimization.

Injection Pressure	State	Signal	Extraction Level (%)	Cumulative Extraction Level (%)	Residual Oil Volume (mL)
15 MPa	Stewing well 50 h	3618.255	——	0.00	0.645
	13 MPa	3488.829	3.58	3.58	0.622
	10.5 MPa	3423.810	1.79	5.37	0.610
20 MPa	Stewing well 50 h	3593.57	——	0.00	0.641
	17 MPa	3343.726	6.95	6.95	0.596
	14 MPa	3232.92	1.74	8.69	0.576
25 MPa	Stewing well 50 h	3557.01	——	0.00	0.634
	21 MPa	3362.14	5.48	5.48	0.599
	17.5 MPa	3215.02	4.13	9.61	0.573

By converting the injection volume into PV volume, the recovered oil volume and the recovery degree under different injection volumes can be obtained, and the results are shown in Table 9 and Figure 16. The CO_2 injection volumes of 0.33 PV, 0.44 PV, and 0.542 PV (Table 9) correspond to the system pressures of 15, 20, and 25 MPa, respectively, and the recovery degrees are 5.37, 8.69, and 9.61%, respectively. With the increase in the injection volume, the recovery degree gradually increases, and the rate of increase in the preferred injection volume of 0.44 PV becomes slower.

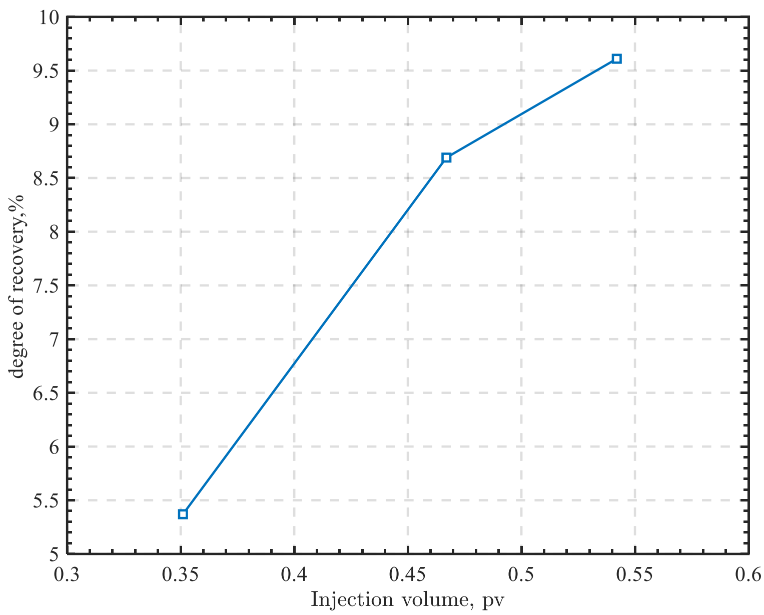

Figure 16. Map of the degree of extraction of different injected PVs.

Table 9. Degree of extraction for different injection volumes.

Injection Pressure MPa	Injection Volume mL	Injection Volume Change to PV Volume	Oil Recovery mL	Extraction Level %
15	0.351	0.33	0.035	5.37
20	0.467	0.44	0.065	8.69
25	0.542	0.51	0.061	9.61

4. Conclusions

1. The on-line NMR huff and puff experiment established in this paper makes up for the shortcomings of the current research on the shale oil huff and puff process, and based on the on-line NMR technology, can realistically simulate the whole huff and puff process of mines under the condition of full closure.

2. The experiment carries out the optimization of CO_2 injection and throughput process parameters. The best stewing time for the first round is 55 h, the best stewing time for the second round is 23–25 h, the best stewing time for the third round is 20–22 h, and the best stewing time for the fourth round is 15–19 h.

3. From the analysis of the extraction degree of the four rounds of CO_2 huff and puff, it can be seen that the first three huff and puffs were obvious, and each round accounted for 56.4%, 28.7%, and 10.7% of the cumulative extraction degree of the four rounds, respectively, and the optimal number of huff and puff rounds were recommended to be three. The CO_2 injections were 0.33 PV, 0.44 PV, and 0.542 PV, which corresponded to an extraction degree of 5.37, 8.69, 9.61%, and the preferred injection volume was 0.44 PV.

Author Contributions: Conceptualization, Y.G. and J.S.; methodology, Y.G.; drawings, S.L.; validation, D.L. and J.S.; formal analysis, Y.G.; investigation, D.L.; resources, D.L.; data curation, L.C.; writing—original draft preparation, Y.G.; writing—review and editing, Y.G.; supervision, J.S.; project administration, J.S.; funding acquisition, J.S. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Science and Technology Major Project during the 13th Five-Year Plan under grant number 2016ZX05060004.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data generated or analyzed during this study are included in the published article.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Lei, Q.; Xu, Y.; Cai, B. Progress and Prospects of Horizontal Well Fracturing Technology for Shale Oil and Gas Reservoirs. *Pet. Explor. Dev.* **2022**, *49*, 166–172. [CrossRef]
2. Lei, Q.; Weng, D.; Xiong, S. Progress and Development Directions of Shale Oil Reservoir Stimulation Technology of China National Petroleum Corporation. *Pet. Explor. Dev.* **2021**, *48*, 1035–1042. [CrossRef]
3. Zou, C.; Li, J.; Yang, S. Theory, Technology, and Prospects of Conventional and Unconventional Natural Gas. *Pet. Explor. Dev.* **2018**, *45*, 13. [CrossRef]
4. Hamza, A.; Hussein, I.A.; Al-Marri, M.J.; Mahmoud, M.; Shawabkeh, R.; Aparicio, S. CO_2 enhanced gas recovery and sequestration in depleted gas reservoirs: A review. *J. Pet. Sci. Eng.* **2021**, *196*, 107685. [CrossRef]
5. Striolo, A.; Cole, D.R. Understanding shale gas: Recent progress and remaining challenges. *Energy Fuels* **2017**, *31*, 10300–10310. [CrossRef]
6. Wang, Y.; Wang, Z.; Zhang, Z.; Yao, S.; Zhang, H.; Zheng, G.; Luo, F.; Feng, L.; Liu, K.; Jiang, L. Recent techniques on analyses and characterizations of shale gas and oil reservoir. *Energy Rev.* **2024**, *3*, 100067. [CrossRef]
7. Fu, L.; Shao, Y.; Shao, M.; Zhu, T.; Li, X.; Yang, Z.; Zou, J.; Fan, M.; Liao, K. Application and Research Progress of CO_2 Stimulation Technology in Unconventional Oil and Gas Reservoirs: A Review and Prospect. *Energy Fuels* **2023**, *37*, 19400–19418. [CrossRef]
8. Shang, S. *Study on the Mixture of Supercritical CO_2 and Cosolvent to Improve Shale Oil Recovery*; China University of Petroleum: Beijing, China, 2020.

9. Wang, Q.; Li, Z.; Qian, M.; Jiang, Q.; Cao, T.; Liu, P.; Bao, Y. Movable oil extraction from shale with supercritical carbon dioxide. *Pet. Geol. Exp.* **2020**, *42*, 646–652.
10. Sambo, C.; Liu, N.; Shaibu, R.; Ahmed, A.A.; Hashish, R.G. A technical review of CO_2 for enhanced oil recovery in unconventional oil reservoirs. *Geoenergy Sci. Eng.* **2023**, *221*, 111185. [CrossRef]
11. Lin, C.; He, J.; Liu, Y.; Mao, J.; Li, X.; Yang, X.; Zhao, J. Quantitative characterization of cracking process in oil shale using micro-CT imaging. *Arab. J. Geosci.* **2022**, *15*, 301. [CrossRef]
12. Tianshou, M.; Ping, C. Study of meso-damage characteristics of shale hydration based on CT scanning technology. *Pet. Explor. Dev.* **2014**, *41*, 249–256.
13. Kang, Z.; Zhao, Y.; Yang, D. Review of oil shale in-situ conversion technology. *Appl. Energy* **2020**, *269*, 115121. [CrossRef]
14. Alfarge, D.; Wei, M.; Bai, B. Factors affecting CO_2-EOR in shale-oil reservoirs: Numerical simulation study and pilot tests. *Energy Fuels* **2017**, *31*, 8462–8480. [CrossRef]
15. Zhu, C.; Sheng, J.; Ettehadtavakkol, A.; Li, Y.; Gong, H.; Li, Z.; Dong, M. Numerical and experimental study of enhanced shale-oil recovery by CO_2 miscible displacement with NMR. *Energy Fuels* **2019**, *34*, 1524–1536. [CrossRef]
16. Wang, H.; Lun, Z.; Lv, C.; Lang, D.; Luo, M.; Zhao, Q.; Zhao, C. Nuclear-magnetic-resonance study on oil mobilization in shale exposed to CO_2. *SPE J.* **2020**, *25*, 432–439. [CrossRef]
17. Liang, D.; Lun, Z.; Lyu, C.; Wang, H.; Zhao, Q.; Sheng, H. Nuclear magnetic resonance experimental study of CO_2 injection to enhance shale oil recovery. *Pet. Explor. Dev.* **2021**, *48*, 702–712. [CrossRef]
18. Fan, L.; Chen, J.; Zhu, J.; Nie, X.; Li, B.; Shi, Z. Experimental study on enhanced shale oil recovery and remaining oil distribution by CO_2 flooding with nuclear magnetic resonance technology. *Energy Fuels* **2022**, *36*, 1973–1985. [CrossRef]
19. Liu, J.; Xie, R.; Guo, J.; Xu, C. Study of nuclear magnetic resonance response mechanism in shale oil and correction of petrophysical parameters. *Fuel* **2024**, *358*, 130162. [CrossRef]
20. Xu, F.; Jiang, H.; Liu, M.; Jiang, S.; Wang, Y.; Li, J. NMR-Based Analysis of Fluid Occurrence Space and Imbibition Oil Recovery in Gulong Shale. *Processes* **2023**, *11*, 1678. [CrossRef]
21. Fallavena, V.L.; de Abreu, C.S.; Inácio, T.D.; Azevedo, C.M.; Pires, M.; Ferret, L.S.; Fernandes, I.D.; Tarazona, R.M. Determination of mineral matter in Brazilian coals by thermal treatments. *Fuel Process. Technol.* **2014**, *125*, 41–50. [CrossRef]