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Thermodynamic Effects of Cycling Carbon Dioxide injectivity in Shale Reservoirs.

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Abstract

Carbon dioxide injectivity has always been considered as one of the optimum enhanced recovery techniques, especially in tight reservoirs regarding the feasible mobilization of gas through porous media. To have a better understanding of carbon dioxide injectivity performances, it would be of importance to consider crucial parameters and their effects on the carbon dioxide adsorption and oil recovery factor. In this paper, the profound impact of crucial parameters such as temperature, pressure, carbon dioxide soaking time, and core stimulation on the oil recovery enhancement were investigated. Moreover, the considerable influence of pressure and temperature on the carbon dioxide adsorption capacity storage were performed and analyzed. According to the result of this experiment, temperature increase led to reducing carbon dioxide storage capacity, which has a reverse pattern with oil recovery factor by increasing temperature. When the core samples were unstimulated, the oil recovery factor has higher than stimulated core samples. Furthermore, pressure increase resulted in the carbon dioxide storage capacity enhancement, which has a similar increase pattern with oil recovery factor by increasing pressure. The maximum carbon dioxide storage capacity is 91% and 90% at the pressure of 1500 psi and temperature of 20 °C respectively. Soaking time rising between oil and carbon dioxide led to producing more oil volume.

Keywords; Carbon Dioxide Storage Capacity; Oil Recovery Factor; Soaking Time; Core stimulation; Shale Reservoirs

1. Introduction

Carbon dioxide capture and storage (henceforth; CCS) or carbon dioxide sequestration is one of the essential processes that is used in petroleum industries. It has used as a wide variety of techniques and advanced procedures such as isolation, extraction, and carbon dioxide emission storage from numerous industrial plants instead of its release to the atmosphere (Davaranpanah and Mirshekari, 2019b; Ebadati et al., 2018; Mazarei et al., 2019; Davaranpanah et al., 2018). This process can have a mutual impact both on the environmental aspects and provide required carbon dioxide for thermal injectivity patterns in oil production wells. Therefore, optimum carbon volumes storage from industrial plants would reduce unnecessary expenses of providing carbon dioxide that is used for thermal injections (Benson and Orr, 2008; Huijgen and Comans, 2003; Pan et al., 2020). Porous media effective thermal conductivity is one of the significant phenomena in thermal recovery methods, which should be addressed clearly and crucial parameters that impact this phenomenon should be taken into consideration. Xiao et al. (2019) proposed a probability model to consider porosity, relative roughness, fractal dimensions, and pores diameters (maximum and minimum) impact on the porous media effective thermal conductivity. They concluded that tortuosity fractal dimension and relative roughness increase has led to the decrease of porous media effective thermal conductivity (Xiao et al., 2019a). Xiao et al. (2019) proposed a novel fractal solution to consider the Kozney-Carman constant and permeability of the fibrous porous medium. According to their results, absolute permeability would be increased by the increase of porosity and particle diameter; however, it is decreased with the tortuosity fractal dimension increase. Moreover, Kozney-Carman constant has increased with the tortuosity fractal dimension increase. This model would help to have a better understanding of fluids mobilization in porous medium which can be extended to carbon dioxide transport in porous medium and how to predict the relationship between permeability and other

parameters in shale reservoirs (Xiao et al., 2019b). Long et al. (2018) proposed a perforation-erosion model to predict specific erosion parameters that are depended on the abrasion mechanisms. They found that the perforation diameter and discharge coefficient alternative increase assumptions in some of the conventional models would be inappropriate. To provide a successful limited entry treatment, they incorporate the model with a nonplanar hydraulic-fracturing simulator to anticipate relevant perforation-number distributions at different clusters. This can generates uniform fractures and relative fluid distribution which can be used in injectivity scenarios (Long et al., 2018).

Carbon dioxide (CO₂) injection has been widely used in numerous oil and gas fields regarding its high potential and more mobilization of this gas in low permeable areas to push trapped oil to the surface (Vasco et al., 2020; Varadharajan et al., 2019; Zhang et al., 2017; Araújo et al., 2017). Possible carbon dioxide storage can be considered geologically, which provided novel challenges in operational and remediation performances (Jiang et al., 2019; Alper and Orhan, 2017; Aminu et al., 2017; Zhang and Huisin, 2017). Although, CO₂ flooding is considered as one of the efficient techniques in the oil recovery enhancement, and it could be administered as a potential mechanism to increase the trapped oil sweep efficiency displacement (Bayat et al., 2016; Bikkina et al., 2016; Kumar and Mandal, 2017). In the unconventional reservoirs, especially shale reservoir, due to the higher interaction between carbon dioxide and formation fluids, this technique is defined as an efficient way to shale rock adsorption (Alfarge et al., 2018; Elwegaa et al., 2019; Burrows et al., 2020; Pan et al., 2018; Harrison et al., 2017). To have a better understanding of carbon dioxide injectivity performances, it is necessary to consider crucial parameters and their effect on the carbon dioxide adsorption and oil recovery factor. Cycling carbon dioxide is usually referred to as the huff-n-puff method that can provide higher oil recovery factor in shale reservoirs (Li et al., 2017; Sun et al., 2019; Hamdi et al., 2018). The interaction of carbon dioxide with formation fluid

has led to reduce oil viscosity and enhance the mobility ratio. The profound impact of crucial parameters such as temperature, pressure, carbon dioxide soaking time, and core stimulation on the oil recovery enhancement should be taken into consideration before performing recovery processes (Zhang et al., 2019; Li et al., 2019; Alfarge et al., 2018; Pranesh, 2018).

Carbon dioxide adsorption capacity in shale reservoirs could be affected by several parameters such as carbon dioxide injection pressure, temperature and shale particle sizes. Therefore, regarding the influence of different fluids interaction in the reservoir, carbon dioxide has provided the optimum condition in shale reservoirs. Gamadi et al. (2013) investigated the different soaking period effect on the oil recovery factor in one cycle. They concluded that near the immiscible condition pressure of 1000 psi, there is no significant difference between the soaking time of two or three days. However, in this paper, we investigated the considerable influence of soaking time and increase the number of cycles simultaneously. This simultaneous experiment would be another limitation of this paper as shale core samples would be broken in higher cycles number. Therefore, we aimed to consider the simultaneous impact of soaking time and cycling numbers which is taken into consideration in this study (Gamadi et al., 2013).

Gamadi et al. (2014) investigated the potential impact of cyclic carbon dioxide injection to enhance oil recovery from shale reservoirs. One of their results is related to consider different pressure injection ranges between 850-3500 psi on the oil recovery factor in just one cycling injection (Gamadi et al., 2014). Then, they consider more cycles of carbon dioxide injection up to six cycles. However, in this study, we set aside on the more cycling injection (4-10 cycling numbers), which is provided with some pressure limitations as shale core samples were being broken after nine or ten cycling samples. Therefore, one of the chief aims of this study to concentrate on the cycling number of carbon dioxide injection rather than 1-6 cycles which was done before by Gamadi et.al

(2014). Moreover, they concluded that at 1200 psi, there is highest oil recovery was obtained, and after that, it has reached a plateau. Therefore, we set aside our pressure ranges up to 1250 psi as it has not any significant effect after this pressure. Davarpanah and Mirshekari (2019) proposed unipore diffusion and modified unipore diffusion mathematical model to compare the methane and carbon dioxide at different pressure ranges in two shale reservoirs(Davarpanah and Mirshekari, 2019a). They concluded that pressure increase in carbon dioxide injectivity scenarios has led to oil recovery increase. However, they consider non-cyclic carbon dioxide injection, and in this paper, different injectivity scenarios are discussed by the increase of carbon dioxide cycles number.

We aimed to consider the significant effect of crucial parameters of temperature, pressure, carbon dioxide soaking time, and core stimulation on the oil recovery enhancement in the cyclic carbon dioxide injectivity performances as a limited number of studies have considered the issue. Moreover, the considerable influence of pressure and temperature on the carbon dioxide adsorption capacity storage were performed and analyzed.

2. Materials and Methods

2.1. Materials

In this experiment, the shale samples outcrops were chosen from Pazanan oilfield in the south-west of Iran. The samples lengths are 2 inches and the average outer diameter of one inch. The permeability ranges for these core samples are varied from 0.2-0.4 mD. The porosity of the core shale samples is varied between 1.96 % and 2.74%. Due to the XRD analysis, shale core samples consisted of 18% quartz, 53% illite, 8% calcite, 13% dolomite, 5% chlorite and 3% of other minerals such as smectite, orthoclase, and marcasite. As the number of cycles was between 4-10 cycles, after finishing the test for each parameter, there are lots of fractures in the cores. Therefore,

we do not reuse core samples. Furthermore, some of the cores were broken in the processes, and we repeat the tests with new core samples. The number of cores that were used in this experiment was about 40 core samples. Helium and carbon dioxide with the 99.9 % purity was used as a gas supply which was provided by the high-pressure cylinder. The crude oil that was used in this procedure had the 67 cP viscosity. Average composition for the provided crude oil is described statistically in Table 1.

Table 1. Crude oil Composition

Composition	Mole%	Composition	Mole%
C₁	21.51	C₈	3.14
C₂	7.65	C₉	4.25
C₃	4.95	C₁₀	4.03
nC₄	2.45	C₁₁	4.97
iC₄	3.68	C₁₂₊	5.36
nC₅	3.85	CO₂	0.84
iC₅	4.22	H₂S	0
C₆	5.16	N₂	0.3
C₇	23.64		

2.2. Experimental apparatus

The schematic experimental apparatus of carbon injection is depicted in Figure 1. It was designed to provide the cyclic injection of carbon dioxide in shale core samples. High-pressure gas was injected into the system to measure carbon dioxide adsorption by the volumetric method. As can be seen in Figure 1, to calculate the adsorption, a reference cell is required in the system as the carbon dioxide was expanded in this cell and pressure was measured accordingly. Carbon dioxide injection procedure steps are explained in more detail in Table 2.

Table 2. Carbon dioxide injection and adsorption procedure steps

Step	Description
1	To measure the pore volume, shale core samples were put in the high-pressure vessel, which is contained the crude oil and then they were placed in the high-temperature oven. Finally, the pore volume was obtained before and after the saturation by weighing the cores. It can help to measure the oil recovery factor.
2	The saturated shale core sample was placed in a sealed high pressurized vessel for 12 hours in a water bath
3	In this step, carbon dioxide was injected into the pressurized vessel, and when the temperature and pressure reached to their designed value, carbon dioxide was left to be soaked.
4	When the soaking was finished, pressure gauges were closed, and shale core sample was exited.
5	Oil recovery factor was measured according to the core weight changes.
6	Again, after vacuuming the core sample cell, new carbon dioxide cycling injection was started until the incremental recovery factor has reached less than 1%.
7	To decrease the required time for carbon dioxide diffusion during the adsorption process, the shale core sample was rubbing out in micro and nanoparticles.
8	After vacuuming the cells for 12 hours, small shale particles were placed in the shale core cell and to occupy the void spaces between them helium gas was used. It should be considered in the calculation of adsorption.
9	Carbon dioxide was reached a designed pressure, and then it is expanded to the shale core cell.

Figure 1. Schematic experimental apparatus of carbon injection

Carbon dioxide adsorption is performed according to the volumetric adsorption measurement. Firstly, shale core samples were pulverized into micro-sized particles to decrease the carbon dioxide required time to diffuse to the matrixes. Next, micro-sized particles were placed in a mesh screen to prevent particles suction into the sample cell during vacuum. The vacuum time is 12 hours, and helium gas was used to measure void spaces between particles. Since then, carbon dioxide was injected to the reference cell to reach the determined pressure and expanded to the sample cell. When the pressure in both cells had reached equilibrium (which might be taken three to eight days that is related to the interaction of carbon dioxide and shale particles), and then equilibrium pressure

value was used to measure adsorption capacity. Adsorption isotherm generated in the temperature of 50 °C by the utilization of 48 µm particle sizes.

3. Results and Discussion

3.1. Pressure impact

Regarding the specific properties of carbon dioxide in liquid or gas phases, which might be related to the carbon dioxide in each phase, we define injection pressure ranges from 250-1250 Psi to see what exactly happened. This is due to the carbon dioxide density when it is in the gas phase that can mobilize more conveniently through the pores in higher injection pressures. These injection pressure ranges give us the sensitive visualization from relative high pressures to high supercritical pressures which can potentially influence the oil recovery factor. This oil recovery increase is due to the reduction of carbon dioxide, which simplified its mobilization through pores. To explain the carbon dioxide soaking pressure impact on the oil recovery performances, we consider five different pressures of 250, 500, 750, 1000, and 1250 psi in 6 hours in the assumed well temperature of 50 °C. As it is evident in Figure 2, pressure increase resulted in rising the number of cycling injection. Moreover, pressure increase from 250 psi to 750 psi has changed the oil recovery factor slightly; however, after 750 psi, the recovery factor has increased dramatically as the number of cycling injection was increased. Consequently, the increase in oil recovery factor in 1250 psi is related to the natural fractures excessive stimulation of the shale cores. This excessive stimulation led to producing more fractures in the injection pressure of 1350 psi. This was resulted in the higher carbon dioxide surface area with shale fractures and increase the oil recovery factor. Furthermore, it was observed that for each injection pressure, after a specific number of cycle's progression, fracture stimulation has become more severe. Thereby, the oil recovery factor was slightly increased after each number of cycles. In the injection pressure of 1250 psi, after eight

cycles, fracture stimulation was become more sever and oil recovery factor was increased with less inclination. Gamadi et al. (2014) investigated the potential impact of cyclic carbon dioxide injection to enhance oil recovery from shale reservoirs. They consider the effect of different pressure injection ranges between 850-3500 psi on the oil recovery factor in just one cycling injection (Gamadi et al., 2014). Then, they consider more cycles of carbon dioxide injection up to six cycles. However, in this study, we set aside on the more cycling injection (4-10 cycling numbers), which is provided with some pressure limitations as shale core samples were being broken after nine or ten cycling samples.

Figure 2. Pressure impact on the oil recovery performances

3.2. Temperature Impact

To compare the significant influence of temperature on the oil recovery enhancement, it is essential to provide different temperature ranges that are lower and same as field temperature and compare the results. To do this five temperatures were designed from 20-60 °C in the carbon cycling process

in the soaking time of 6 hours and confining pressure of 1250 psi. As can be seen in Figure 3, temperature increase regarding the expansion of the pores at higher temperatures resulted in crude oil viscosity reduction. As the temperature increased, pore sizes would be increased due to the gradual expansion of shale-rock grains. In this situation, the consolidation of grains would decrease as the cementing materials had weakened in higher temperatures, and more natural fractures would be created. At 60 °C, the oil recovery factor was reached its maximum value of 53%, rather than other temperatures, and by increasing temperature, the number of carbon dioxide cycling had increased. Therefore, the oil recovery factor had been increased by the temperature increase. However, in the first cycles, regarding the difference between average pore sizes and core, at 20 °C, there might be a steep rise in oil production rather than other temperatures. It was resulted in the presence of different core natural fractures that might be attributed to some errors in experimental procedures. This issue would be neglected during the cycle progressions as it was affected by viscosity reduction and pore size expansion. Moreover, due to the cyclic carbon dioxide injection, shale core samples color is changed in each cycle. It is indicated that carbon dioxide can diffuse to the shale core nanopores and as a result to mobilize and produce oil in the outlet of the core samples.

Figure 3. Temperature impact on the oil recovery performances

3.3. Soaking time

The required time for the interaction of carbon dioxide with rock and formation fluid before the production is expressed as the soaking time. As it is plotted in Figure 4, increasing the soaking time between oil and carbon dioxide resulted in more oil volume production. The experiments were done at 50 °C and confined pressure of 1250 psi. There were not any significant changes between 12 hour and 24 hours of soaking time on oil recovery enhancement. It is indicated that increasing soaking time from 12 hours to 24 hours would not be beneficial enough, and it is non-producing time as oil recovery increase is very small. Thereby, we did not perform the experiments for 48 hours and more as it would be more costly, and there is no significant difference in the oil recovery factor. The maximum recovery factor after 24 hours of carbon dioxide soaking time with oil is about 60%. Gamadi et al. (2013) investigated the different soaking period effect on the oil recovery factor in one cycle. They concluded that near the immiscible condition pressure of 1000

psi, there is no significant difference between the soaking time of two or three days. However, in this paper, we investigated the considerable influence of soaking time and increase the number of cycles simultaneously (Gamadi et al., 2013). In this paper, as there is no difference between 12 hours and 24 hours soaking time on the oil recovery enhancement, we did not continue the experiments as it was not economically profitable which was proved by Gamadi et al. (2013) too.

Figure 4. Impact of soaking time on the oil recovery performances

3.4. Core stimulation impact

As some of the shale reservoirs are fractured, it is vitally essential to consider the core stimulation impact on the oil recovery enhancement and would help to manage the carbon dioxide storage. Experiments were performed at 50 °C and confined pressure of 1250 psi during the injection of 60 cP crude oil for 6 hours. As fractured shale cores might be broken during cyclic carbon dioxide injection, it might have some errors in the stimulated results because small shale chunks were being lost and it is indicated higher oil production. It might be resulted to terminate the cycling injection

before reaching the maximum oil recovery. As can be seen in Figure 5, if the core samples were unstimulated, the oil recovery factor has higher than stimulated core samples. Moreover, regarding the high conductivity of fractures, the oil recovery factor was increased fast in the first cycling injection. These high oil recoveries might affect the conclusive decision about the efficiency of cyclic carbon dioxide injection for both stimulated and unstimulated core samples. On the other hand, it is concluded that cyclic carbon dioxide injection would play a substantial role in the oil recovery enhancement from shale reservoirs.

Figure 5. Impact of core stimulation on the oil recovery performances

3.4. Carbon dioxide adsorption capacity

In this part, we investigated the considerable influence of temperature and carbon dioxide injection pressure on the carbon dioxide adsorption capacity. Shale cores adsorption isotherm is plotted in Figure 6 at 50 °C, which indicated the shale samples adsorption behavior. Effect of temperature and carbon dioxide injection pressure on the carbon dioxide adsorption is statistically depicted in

Tables 3 and 4. According to table 3, five temperatures were designed from 20-60 °C at the confining pressure of 1250 psi. As can be seen, temperature increase leads to reduce carbon dioxide storage capacity, which has a reverse pattern with oil recovery factor by increasing temperature. Thereby, it is of importance to determine the carbon dioxide storage capacity before recovery processes as it can define the oil recovery processes. The maximum carbon dioxide storage capacity is 90% at the temperature of 20 °C.

Figure 6. Shale cores adsorption isotherm at a different relative pressure

Table 3. Temperature impact on the carbon dioxide storage capacity

Temperature (°C)	Carbon Dioxide Adsorption, scf/ton
20	90
30	88
40	85
50	82
60	80

According to table 4, six pressures were designed from 250-1500 psi at the temperature of 50 °C. As can be seen, pressure increase leads to rising carbon dioxide storage capacity, which has a similar increase pattern with oil recovery factor by increasing pressure. Thereby, it is of importance to determine the carbon dioxide storage capacity before recovery processes as it can define the oil recovery processes. The maximum carbon dioxide storage capacity is 91% at the pressure of 1500 psi. During the recovery processes, it should be noted that extreme pressures might deform the reservoir heterogeneity and fractures. Therefore, the oil recovery factor would be decreased.

Table 4. Pressure impact on the carbon dioxide storage capacity

Pressure (Psi)	Carbon Dioxide Adsorption, scf/ton
250	80
500	81
750	83
1000	85
1250	87
1500	91

4. Conclusion

It is of importance to determine the carbon dioxide storage capacity before recovery processes as it can define the oil recovery processes. The main conclusion of this study are as follows;

- The temperature increase leads to reduce carbon dioxide storage capacity, which has a reverse pattern with oil recovery factor by increasing temperature.
- Pressure increase leads to rising carbon dioxide storage capacity, which has a similar increase pattern with oil recovery factor by increasing pressure.

- When the core samples were unstimulated, the oil recovery factor has higher than stimulated core samples.
- Increasing the soaking time between oil and carbon dioxide resulted in more oil volume production

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