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The Significant Influence of Carbon Dioxide Dissolution in Oil on Asphaltene Aggregation.

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Abstract

The primary objective of this study is to analyse the impact of dissolving carbon dioxide in oil on the aggregation of asphaltene and the reduction of oil permeability in sandstones. The study considers various options for oils interaction with carbon dioxide, both in free volume before injection into a porous medium and directly in the porous medium. Moreover, the study examines the influence of oil composition on the aggregation of asphaltene. This study delves deeper into the impact of dissolved carbon dioxide on the dispersion of the asphaltene in oil by examining how the oil flows in sandstones. Aggregation of asphaltenes in a porous medium can lead to serious problems such as the obstruction of pores and reduction in rock permeability. This can present a challenge when developing wells for carbon dioxide injection, making it difficult to achieve the desired production and oil recovery rates. It has been established that when oil interacts with carbon dioxide in a free volume before injection into a porous medium, there is a decrease in the relative mobility of oil with dissolved carbon dioxide. This is due to an increase in the volume of flowed oil, the concentration of carbon dioxide dissolved in the oil, as well as a decrease in the permeability of sandstone. The experimental results demonstrate a significant correlation between sandstone permeability and asphaltene aggregate size, indicating that the sizes of these aggregates are comparable to those of small pores. Moreover, it is worth noting that complete flow blockage in sandstones was not observed, even after exposure to oil with dissolved carbon dioxide. It has been proven that the interaction between oil and carbon dioxide within a porous medium leads to the aggregation of asphaltene due to changes in the composition and properties of oil. This phenomenon has been observed during laboratory experiments that involved oil displacement by carbon dioxide rims. As the asphaltene content in the oil composition increases, the formation oil permeability decreases significantly. Moreover, low-permeable formations exhibit a greater decrease in permeability.

Keywords: Asphaltene Aggregation, Carbon Dioxide, Formation Oil Permeability, Oil Mobility, Porous Medium.

1. Introduction

A common method of gas stimulation is to inject carbon dioxide into oil reservoirs, which increases oil recovery in certain conditions compared to water flooding [1-4]. The positive effect of using carbon dioxide is achieved due to its influence on surface phenomena in the reservoir and on the properties of oil, water and reservoir [5-8].

In Russia, extensive research has been conducted on the impact of carbon dioxide on oil, water, and reservoir rocks, as well as methods to increase oil recovery [9-12]. Studies have found that carbonated water containing up to 50% carbon dioxide can significantly enhance oil displacement. Additionally, introducing single slugs of carbon dioxide with varying sizes alternated with water can further improve the process. Testing conducted in regions such as Bashkortostan, Tatars tan, and other parts of Russia has demonstrated the

potential for an increase in the oil displacement coefficient of up to 5-16% under immiscible displacement, and up to 23% under conditions similar to miscible displacement [13-16]. Extensive studies have been conducted to assess the impact of carbon dioxide on the characteristics of oil, water, and reservoir rocks. Through these studies, researchers were able to identify several important aspects of how oil is displaced by water in the presence of carbon dioxide [17-20].

During the dissolution of large amounts of carbon dioxide, asphaltene aggregates in oil, limiting the active use of carbon dioxide [21-24]. The process of asphaltenes aggregation, if taking place in a porous medium, can lead to the blockage of pores, resulting in a significant decrease in rock permeability. This, in turn, poses a challenge during the development of wells for carbon dioxide injection and can make it difficult

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to achieve the desired production and oil recovery rates [25-28]. It is a fact that asphaltenes aggregation can cause complications that need to be addressed with utmost care. Thoroughly studying the interaction between carbon dioxide and high-molecular oil components in the reservoir provides the knowledge to select the most effective chemical reagents confidently. This results in significantly higher efficiency when using carbon dioxide to enhance oil recovery.

The first field experiment in Russia to inject carbonated water into an oil reservoir occurred in 1967 at the Aleksandrovskaya area of the Tuymazinskoye field. In the 1980s, the pilot industrial injection of carbon dioxide was boldly implemented at the Radaevskoye, Kozlovskoye, Elabuga, Olkhovskoye, and Sergeevskoye fields [29-32]. It resulted in a specific effect range of 0.125 to 0.28 tons of additional oil production per 1 ton of injected liquid carbon dioxide. The implementation of carbon dioxide injection into oil reservoirs has been plagued by technological complications [33-36]. Specifically, corrosion of surface and downhole equipment and aggregation of asphaltene in the bottom hole formation zone of injection wells have led to a

decrease in their injectivity. As a result of these challenges, all carbon dioxide injection projects in Russia until the late 1980s and early 1990s were closed [37-40].

The primary objective of this research was to thoroughly examine the effects of carbon dioxide dissolving in oil on two crucial factors - the aggregation of asphaltene and the reduction of oil permeability in sandstones. The study explored various scenarios related to how oil interacts with carbon dioxide, including its behavior in a free volume before injection into a porous medium and its direct interaction within a porous medium. Additionally, the study looked at the influence of oil composition on the aggregation of asphaltene to better understand the underlying mechanisms at play.

2. Materials and Research Methods

The effect of dissolved carbon dioxide on the state of highmolecular components was thoroughly studied through an experimental investigation of three different oil samples gathered from the fields of the Republic of Bashkortostan. The physical properties and composition of the studied samples are given in Table 1.

Table 1: Degassed Oil Properties and Composition.

Parameters	Sample No. 1	Sample No. 2	Sample No.3
Formation temperature, °C	40	40	40
Oil density at standard conditions, Kg/m ³	906	910	832
Dynamic oil viscosity at standard conditions, mPa·s	101,2	47	25,4
Temperature of oil saturated with paraffin, °C	27,5	28	36
- Mass content, %:			
- Asphaltenes;	7,9	4,8	3,3
- Silica gel resins;	18,2	16,8	10,4

2.1. Study of the Influence of the Carbon Dioxide Amount Dissolved in Oil on the Dispersion of Asphaltenes using the Injection Method.

The effect of dissolved carbon dioxide on the dispersion of asphaltenes in oil was studied by injecting it in sandstones [41-44]. In this case, the porous medium acted as a filter (sieve) with pore sizes up to $40\text{--}50~\mu\text{m}$. Oil samples No. 1 and No. 2 were selected for the experiments. The experiments were carried out in an injection installation at a temperature of 40 °C and a pressure of 10 MPa.

To analyze the dispersion of asphaltenes in oil samples, a process was conducted in which up to 20% of the mass of carbon dioxide was dissolved in stages. Following each stage, the oil was passed through sandstones with varying absolute permeabilities, and the mobility of the oil was studied at large pumping volumes. The mobility value was determined by passing a volume of oil through the sandstone that is a multiple of the pore volume (up to 12 pore volumes of oil with carbon dioxide). For reference, the dimensions and physical properties of the sandstones used are provided in Table 2.

Table 2: Dimensions and Properties of Sandstone Samples

Sample No.	Length, cm	Cross-sectional	Porosity, %	Permeability, md	
		area, cm2		Air	Oil
1	3,21	6,07	14,5	27	4
2	3,6	6,38	19,4	345	186

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2.2. Study of Asphaltene Aggregation during Oil and Carbon Dioxide Interaction in a Porous Medium.

The experiments utilized the oil samples listed in Table 1. The temperature of the porous medium did not surpass $31\,^{\circ}\text{C}$ in the presence of carbon dioxide. Additionally, the pressure in the installation was kept at $10\,\text{MPa}$ - which is higher than the saturation pressure of oil.

In practice, the oil comes into contact with a carbon dioxide rim near injection wells and in zones bypassed by the displacement front [45-49]. In this regard, the possibility of contact of oil with carbon dioxide directly in a porous medium was provided during the experiments. When displacing oil from the reservoir model, a rim of liquid carbon dioxide equal to two pore volumes was used.

The reservoir models were compiled using natural sandstone cores with an average absolute permeability of 1.14, 0.37, and 0.074 μm^2 . The cylindrical rock samples had a diameter ranging from 28 to 30 mm. It is important to note that while compiling the reservoir model, rock samples were meticulously selected to ensure that the deviation of permeability in each sample did not exceed 5% of the average permeability of the reservoir model [50-53]. This step was taken to ensure the utmost accuracy and reliability of the results.

Asphaltenes aggregation and dispersion in oil can be better understood by conducting experiments that involve direct contact with liquid carbon dioxide in the porous medium of the injection well's bottom-hole zone. In this regard, the following steps were taken to study this phenomenon:

- Injection of the source oil
- Displacement of oil by a rim of liquid carbon dioxide
- Displacement of the carbon dioxide slug by the original oil
- Injection of source oil.

3. Results and Discussion

3.1. The Influence of the Amount of Carbon Dioxide Dissolved in Oil on the Dispersity of Asphaltenes.

As a base case, oil flow was simulated in each series of experiments. When less than 12 pore volumes of oil passed through the reservoir model, the oil mobility coefficient remained unchainged. Subsequently, oil mobility during the flow through large-volume samples was determined after each stage of carbon dioxide dissolution. The results of these measurements are given in Tables 3 and 4. These tables indicate that samples No. 1 and No. 2 show a noticeable reduction in oil mobility when injected through sandstones at dissolved carbon dioxide mass concentrations exceeding 11% and 6%, respectively. The aggregation of asphaltene causes this reduction [54-57].

Table 3: An Analysis of the Change in Relative Mobility of Oil Sample No. 1 When Pumped through Sandstone Sample No. 1.

Mass concentration of carbon	Relative oil mobility after injecting different pore volumes of fluid through sandstone							
dioxide in oil, %	1	2	4	6	8	10	12	14
0	1	1	1	1	1	1	1	1
2,2	1	1	1	1	1	1	1	1
4,4	1	1	1	1	1	1	1	1
6,7	1	1	1	1	1	1	1	1
9,1	1	1	1	1	1	1	1	1
11,6	1	0,979	0,945	0,906	0,892	0,888	0,828	0,812
15,5	1	0,905	0,801	0,697	0,611	0,53	0,478	0,444
18	1	0,798	0,611	0,463	0,395	0,33	0,278	0,24

Table 4: An Analysis of the Change in Relative Mobility of Oil Sample No. 2 When Pumped through Sandstone Sample No. 2

Mass concentration of carbon	Relative oil mobility after injecting different pore volumes of fluid through sandstone							
dioxide in oil, %	1	2	3	4	5	6	7	8
0	1	1	1	1	1	1	1	1
3	1	1	1	1	1	1	1	1
6	1	0,917	0,917	0,835	0,785	0,74	0,698	0,698
9,1	1	1	1	1	1	1	1	1
12,4	1	1	1	1	1	1	1	1
13,3	1	1	1	1	0,733	0,733	0,667	0,667
14,6	1	1	0,894	0,84	0,801	0,779	0,712	0,712
19,3	1	1	0,73	0,6	0,59	0,571	0,584	0,584
20,5	1	0,863	0,744	0,736	0,614	0,547	0,53	0,478

The experimental results have established that the relative oil mobility is significantly influenced by the volume of oil pumped through sandstone, the content of asphaltenes present in it, and the permeability of the porous medium. In this context, relative mobility refers to the ratio of oil mobility after pumping certain pore volumes of oil containing carbon dioxide through sandstone, to the mobility of the same oil through the same sandstone at the beginning of each series of experiments. As the amount of passed oil and the concentration of carbon dioxide dissolved in the oil increase, and the permeability of the sandstone decreases, the relative oil mobility with dissolved carbon dioxide also decreases. The experimental results indicate that the permeability of sandstone has a significant influence on the outcome. This suggests that the size of asphaltene aggregates is similar

to that of small pores. The flow is not completely stopped during the passage of oil with dissolved carbon dioxide through sandstones.

3.2. The Interaction of Oil and Carbon Dioxide in a Porous Medium

Tables 5-7 present the conclusive findings of the oil composition analysis after being passed through a porous medium with carbon dioxide. It can be inferred from the tables presented that the composition of low-resin oil (sample No. 3) remains unchanged when carbon dioxide is used to displace the oil from highly permeable sandstone. When displacing high-resin oil (sample No. 1) from less permeable sandstone, the composition of the oil undergoes only a slight change.

Table 5: Composition Change in Low-Resin Oil (Sample No. 3) When a Carbon Dioxide Slug is Displaced from a Reservoir Model of $1.14~\mu m^2$ Permeability

Stage No.	Oil sampling condition	Bulk content, %			
		Asphaltene	Silica gel resins	Paraffin	
1	Flow of single-phase oil	3,3	10,4	1,5	
2	Displacement of oil by a rim of carbon dioxide	3,3	10	1,4	
3	Displacement of carbon dioxide slug by oil	3,3	10,6	1,4	
4	Flow of single-phase oil	3,2	10,4	1,5	

Table 6: Composition Change in High-Resin Oil (Sample No. 1) When a Carbon Dioxide Slug is Displaced from a Reservoir Model of 0.074 μm^2 Permeability

Stage No.	Oil sampling condition	Bulk content, %			
		Asphaltene	Silica gel resins	Paraffin	
1	Flow of single-phase oil	7,9	18,2	1,3	
2	Displacement of oil by a rim of carbon dioxide	7,7	18,8	1,3	
3	Displacement of carbon dioxide slug by oil	8,2	20,1	1,2	
4	Flow of single-phase oil	7,9	18,2	1,3	

Table 7: The Relative Oil Mobility after Injection through Sandstone No. 1 When Sample No. 1 is Injected.

Reservoir	Absolute permeability, μm²	Change (decrease) in oil permeability during the f			
model No.		Oil sample No. 3	Oil sample No. 2	Oil sample No. 1	
1	1,14	0	0	3	
2	0,37	0	10	42	
3	0,074	11	25	66	

The displacement of oil by carbon dioxide leads to a significant reduction in the asphaltenes content. When oil comes in contact with carbon dioxide, the asphaltene in the oil tend to aggregate and form deposits in the pores of the reservoir model. This results in an increase in the content of asphaltenes in the injected oil that passes through the reservoir model when it encounters a carbon dioxide rim. High-viscosity oil, moving behind the liquid rim of carbon dioxide, partially displaces asphaltene aggregates from the reservoir model. With an increase in the content of

asphaltenes in the oil composition, the oil permeability of the formation decreases significantly, and a more significant decrease in permeability is observed in low-permeability formations (see Table 7).

4. Conclusions

The analysis of changes in the composition and properties of oil in laboratory experiments on oil displacement by carbon dioxide rims demonstrated that asphaltene aggregates in a porous medium when oil comes into direct contact with carbon dioxide. This does not result in a complete attenuation of the flow. Asphaltene aggregates clog small pores. A highly viscous liquid can extract asphaltene aggregates from porous media.

When it comes to identifying the reasons for the decrease in the injectivity of injection wells whilst injecting carbon dioxide slugs, experimental results will play a significant role in the future. These results will also be crucial in selecting suitable chemical reagents capable of increasing the injectivity of wells and recovering residual oil from zones not covered by displacement after injecting carbon dioxide slugs into the formation. Anticipating such future events, it's necessary to keep in mind the importance of experimental results for making informed decisions.

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