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Contents

Nonequilibrium influence of critical fluids on the properties of heavy oil

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Abstract

The oil industry thrives on sustainable production processes. Traditional oil production and reservoir treatment processes consume large volumes of water. This prompts the search for alternative reservoir treatment methods. Supercritical carbon dioxide (sc-CO_2) is used as a promising solvent and reduces water consumption in wet reservoir treatment oil production. Sc-CO_2 technology does not generate wastewater in the oil production process. This saves a huge amount of water, reduces energy consumption and increases productivity at the same time. Sc-CO_2 technology has now reached a commercial level, including in oil production. Optimization of sc-CO_2 treatment conditions in oil production expands the possibilities of environmentally friendly reservoir development methods. The objective of this work is to determine the optimal conditions for oil recovery using sc-CO_2 as a solvent medium.

The study is aimed at identifying the thermodynamic correlation between sc-CO_2 processing conditions and the characteristics of the sc-CO_2-oil system. The methodology of nonequilibrium thermodynamics was used in this study. The factors studied include temperature, pressure and duration of treatment, covering the ranges of 293-308 K, 6.5-7.2 MPa and 1-2 hours, respectively. The studies, determination of the conditions of the PTV parameters and their impact on oil recovery were carried out in model and real oil-containing systems. In addition, oil extraction and analysis of its characteristics were carried out.

The regularities of the volumetric and phase behavior of heavy oil during interaction with supercritical carbon dioxide (sc-CO_2) at reservoir temperatures and pressures have been studied. In the “heavy oil–sc-CO_2” system, thermobaric conditions for pressure changes during fluid injection into the system are determined. The limiting concentration of sc-CO_2 was determined to obtain maximum swelling of oil. It has been shown that the volume of the heavy phase relative to the volume of the system decreases linearly with increasing concentration of sc-CO_2 in contact with it. The influence of thermobaric factors on the degree of recovery of heavy oil components was assessed using a reservoir model reflecting the process of oil displacement.

Pressure and temperature are the main parameters for processing oil-fluid systems in the sc-CO_2 solvent environment. For model and real systems, comparable oil recovery rates were obtained at solvent pressure (7.2 MPa), formation treatment time (1 h) and formation temperature (308 K). Compared to the traditional wet process of sc-CO_2 treatment, the technology increases oil recovery. In this mode, the energy consumption of the oil formation treatment process is also reduced. The process of pumping sc-CO_2 into the "heavy oil-sc-CO_2" system was studied at the depleted well of the Siyazan field in order to increase the recovery factor of heavy oil. The results obtained are important for the transition to promising technologies for processing hard-to-recover oils. The results can be used to intensify oil production. The environmental and economic benefits of using CO_2 fluid are presented.

Keywords: supercritical fluid processing, heavy and hard-to-recover oil, PVT parameters, non-equilibrium effects, optimal processing conditions, phase behavior, environmental friendliness.

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1. Introduction

Known technologies for oil displacement (flooding, thermal steam action, flow diversion, etc.) do not meet modern requirements. At the same time, the oil recovery factor (ORF) is low and amounts to more than 25%. Therefore, the development of hard-to-recover oil reserves requires the development and application of new hydrocarbon production technologies. This will allow increasing the ORF and reducing the development time of the field. Supercritical carbon dioxide (sc-CO_2) displacement technology can be used in a wide range of thermobaric and physicochemical conditions in the reservoir [1-5].

Crude oil with high viscosity and high asphalt and resin content is called heavy oil. At reservoir temperatures, heavy oil is understood to mean crude oil with a viscosity of more than 50 mPa·s, and heavy oil is crude oil with a viscosity of degassed oil of $1–5 \times 10^4$ mPa·s or more 5×10^4 mPa·s, respectively [6]. The contribution of heavy oil to global oil production and energy has been growing in recent years.

The viscosity of heavy oil in contact with the sc-CO_2 during multi-contact mixing decreases. This occurs due to the mutual dissolution of the components of the heavy oil– sc-CO_2 system. However, data on the dissolution of individual phases and components of oil near critical conditions and high sc-CO_2 concentrations are limited. Meanwhile, mass transfer processes when mixing high-viscosity oils and sc-CO_2 can lead to new effects [7-14].

Sc-CO_2 has low viscosity, low surface tension, high diffusion coefficient and good solubility, especially in oil. Under certain conditions, CO_2 and crude oil can mix. At the same time, the viscosity of formation fluids decreases and their throughput increases. In addition, sc-CO_2 may change the properties of crude oil. These properties include reducing interfacial tension, reducing viscosity, enhancing the migration ability of crude oil, and extracting non-polar components of crude oil. All this ultimately leads to increased oil recovery. In other words, these properties lead to improved permeability when sc-CO_2 is used to displace oil. At the same time, the degree of extraction of heavy components also increases, which leads to increased oil recovery [15].

Injecting fluid into a reservoir is a promising method for increasing oil recovery. The phase states of the mixture of sc-CO_2 and oil components are determined by thermobaric conditions, composition and ratio of the volumes of the components. When sc-CO_2 and oil are miscible, mass transfer occurs between the phases. In this case, the oil can be saturated with sc-CO_2 and the light hydrocarbons of the oil are extracted from the system. The result is a heavy oil and light fluid phase. Depending on the interaction conditions in the "heavy oil– sc-CO_2" system and the method of injection of sc-CO_2 into the reservoir, various processes can occur. They affect oil displacement and oil recovery factor. Analysis of data on phase equilibria, volumetric behavior and properties of the phases of the "heavy oil– sc-CO_2" system show that they significantly affect the oil recovery of the reservoir. Therefore, the study of such patterns involving the injection of sc-CO_2 into the reservoir, affecting increased oil recovery, is an urgent task [1-15].

In practice, oil recovery enhancement methods are divided into two groups: 1) Methods of oil production intensification (MOPI); 2) Methods of enhanced oil recovery (MEOR). In this case, MOPI includes technologies that increase the flow of fluid to the bottom of the production well. Whereas in MEOR methods they influence the development object or part of it, and include residual, unrecovered oil reserves in the development.

Thus, the use of unique properties of solvents in a supercritical state allows to increase the efficiency of the technology of extraction of hard-to-recover oils. And the study of thermobaric regularities of the systems "heavy oil– supercritical solvent" allows to create new highly effective methods of intensification of extraction of high-viscosity oils.

In summary, we can draw a conclusion. The obtained data on supercritical extraction in oil refining and petrochemistry are necessary for control and purification of the environment. Therefore, the development of new, environmentally friendly and energy-saving technologies for oil production and processing is an urgent task.

One of the methods of increasing oil recovery is the displacement of oil using high-pressure CO_2. The purpose of this work is to determine the patterns of change in volumetric and phase behavior, as well as to increase the oil recovery of high-viscosity oil when interacting with sc-CO_2.

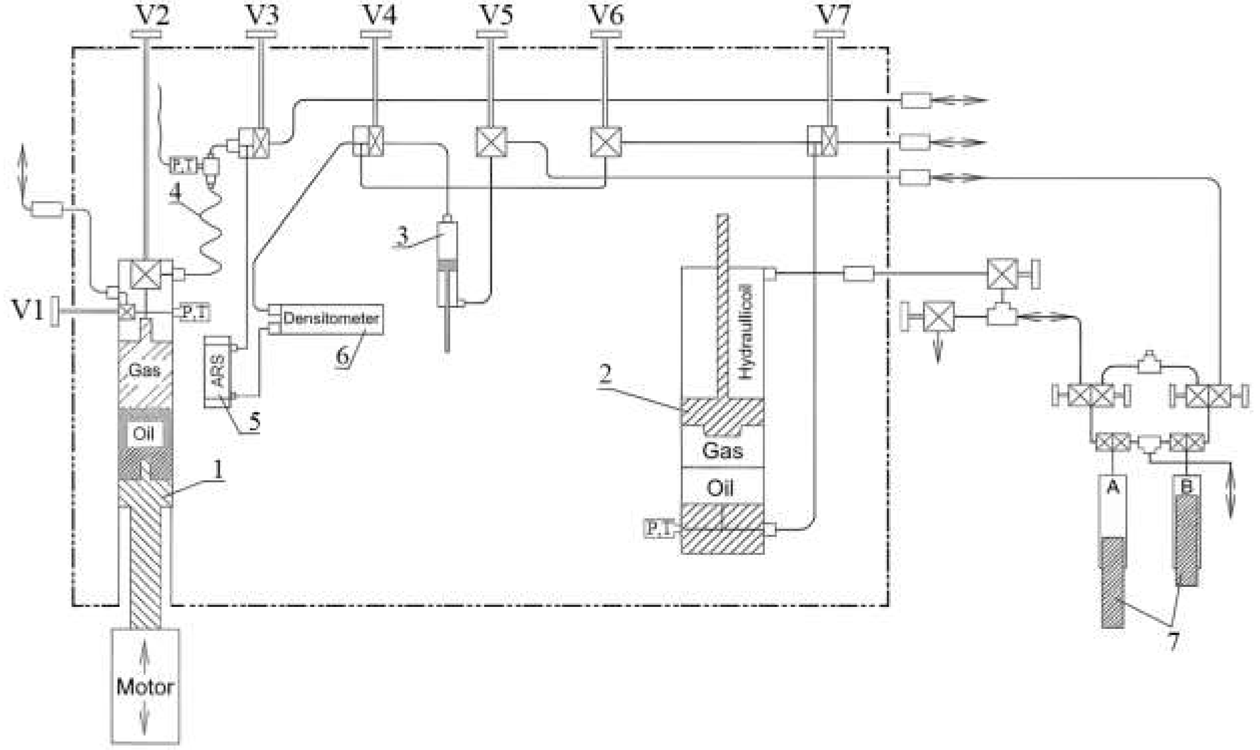
2. Methodological Part

The main properties of the used reservoir oil on average were the following: density of reservoir oil at reservoir pressure 963 kg/m^3, viscosity at reservoir pressure 795–802 mPa·s, concentration (weight %) of paraffin 1.9, resins 49.3, asphaltenes 9.3, water 2.8, mechanical impurities 0.007. The composition of the reservoir oil mainly consisted of C_{9+} residue (95%) and lighter hydrocarbons.

PVT analysis of oil samples was carried out using a *PVT* 3000-L installation (Chandler Engineering, USA) [2]. Laboratory studies of the interaction of sc-CO_2 with high-viscosity oil were carried out in the following optimal thermobaric ranges: 300–308 K and 7–7.5 MPa. The solubility of supercritical carbon dioxide in heavy oil was studied in the temperatures of 300–333 K and pressure range of 7.2–7.5 MPa. The experimental measurement technique for CO_2 solubility in heavy oil was similar to that described in our work [15]. The error in determining solubility was ~1.5%.

The *PVT* installation diagram is shown in Fig. 1. A mixture of formation oil and sc-CO_2 was placed in pump cell 1. Sc-CO_2 was pumped into auxiliary cell 2. Mixing of the components of the "heavy oil–sc-

CO_2” system occurred with valves V6 and V2 open and the pump and auxiliary cells operating in pumping mode. The concentration of sc-CO_2 in the mixture was monitored volumetric method. Thus, the process of one-time mixing of the components was reproduced.



Figuire 1. Installation diagram of *PVT* 3000-L: V1–V7 – needle valves; 1 – pump cell; 2 – auxiliary cell with a piston; 3 – minicell; 4 – capillary viscometer; 5 – ultrasonic solid phase registration system; 6 – digital density meter; 7 – dual cylinder digital pump.

In the mixture with formation oil, the concentration of sc-CO_2 fluid was changed in the range of 10–30 wt.%. At a concentration of sc-CO_2 of 10 wt.%, 300 K and 7 MPa, complete miscibility of the components did not occur. In this case, the oil mixture was separated into a light sc-CO_2 and a heavy oil phase. The volume of the heavy phase was determined by pumping the mixture from the pump to the auxiliary cell. When the heavy oil phase entered capillary viscometer 4, a jump in viscosity was recorded. The cell volume corresponding to this jump was the volume of the heavy phase. The volume of the light phase was calculated from the difference between the volumes of the mixture and the heavy phase.

Studies of phase relationships in the “heavy oil– sc-CO_2” system were carried out in a *PVT* cell [2,3]. *PV* measurements were carried out under isothermal conditions with a decrease in reservoir oil pressure. Thus, the saturation pressure, relative volume, density, compressibility coefficient and specific volume are determined. The saturation pressure is determined by the characteristic break in the *PV* isotherms of the phases. Experiments on displacing oil with carbon dioxide fluid were carried out on a laboratory installation, the diagram of which is shown in Fig. 2.

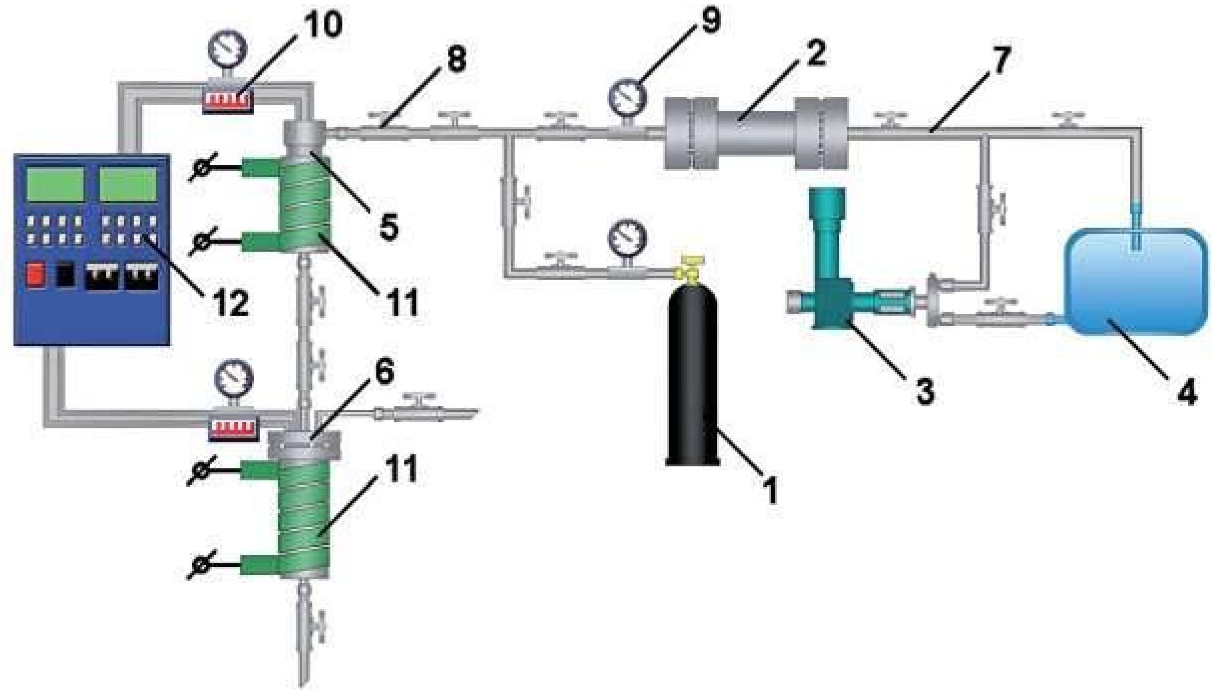


Figure 2. Scheme of the experimental stand for hydrocarbon extraction using supercritical fluid extraction: 1 – container with CO_2 gas; 2 – high pressure cylinder with piston; 3 – high pressure water pump; 4 – water container; 5 – extractor; 6 – separator; 7 – pipeline; 8 – shut-off valves; 9 – pressure sensor; 10 – temperature sensor; 11 – heater; 12 – automation unit.

CO_2 gas from a source (cylinder) is fed to the *PVT* unit and there it is compressed into a supercritical fluid at the critical point (7.38 MPa and 304.1 K) (Fig. 3). Then the sc-CO_2 is pumped into the pipeline of the unit simulating a model of the system of hard-to-recover heavy oil containing sc-CO_2. In such a system, the CO_2 remained in the form of a supercritical fluid.

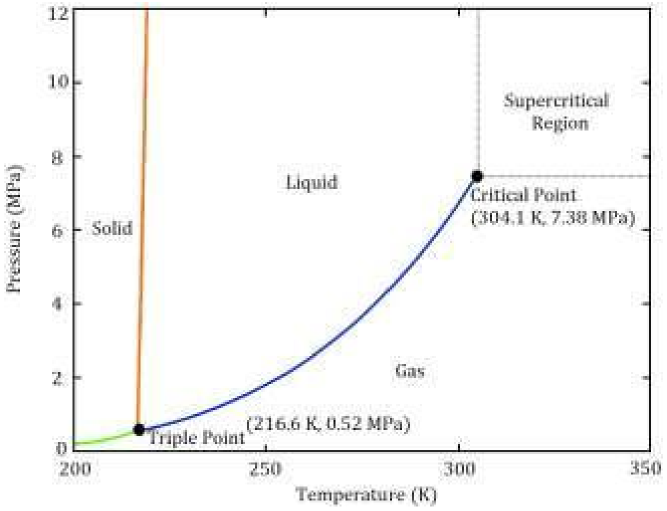


Figure 3. Phase diagram of CO_2.

3. Results and discussion

The lag in the application of technologies in the oil-producing and refining industries is associated not only with material and financial problems. There are also no sufficient scientific and practical results that can significantly change their technological design. Such results include data obtained using supercritical fluid technology in “heavy oil– sc-CO_2” systems. The patterns of changes in the volumetric and phase behavior of high-viscosity oil when interacting with sc-CO_2 have not been systematically studied previously.

3.1. PVT Properties of Fluids

The dependences of CO_2 solubility on temperature (pressure) at different pressures (temperatures) in heavy oil differ from each other. The solubility of CO_2 decreased monotonically depending on temperature at various pressures in the studied oil samples. The results of the experiments are shown in Fig. 4.

A similar dependence on temperature occurs for super-heavy oil [6,15,16]. In contrast, the solubility of CO_2 in heavy oil increases with increasing pressure at different temperatures. Near reservoir conditions, these thermobaric dependences of CO_2 solubility for different heavy oil samples differ little from each other.

When using sc-CO_2, the concentration dependences of the phase volume change have their own characteristics. Let us consider the change in the volumes of oil mixtures under various thermobaric conditions in the “heavy oil– sc-CO_2” system.

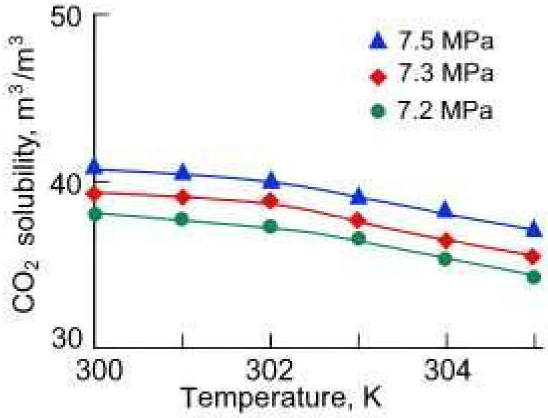


Figure 4. Dependence of CO_2 solubility on temperature at 7.2–7.5 MPa in heavy oil.

As stated in the methodical part, CO_2 has a moderate (T_{cr} = 304.1 K) critical temperature and critical pressure (P_{cr} = 7.38 MPa). Near the critical point, CO_2 mixes well with various organic solvents, including heavy oil. Increasing the critical pressure of CO_2 above 7.5 MPa does not significantly affect the dissolving properties of sc-CO_2 in the “heavy oil– sc-CO_2” system. Based on this, typical experimental results at 7.2–7.5 MPa are given below.

Taking into account the above, the concentration dependences of the volume change below are optimal data. These results were mainly obtained by displacing oil with CO_2 fluid in the pressure range of 7.2-7.5 MPa and temperatures of 303–313 K, oil viscosity of 800 mPa·s and formation permeability of 0.2 μm^2.

The dependence of the ratios of the volumes of oil mixtures on the concentration of sc-CO_2 (10-75 wt.%) at 7.2–7.5 MPa and 303 K is shown in Fig. 5.

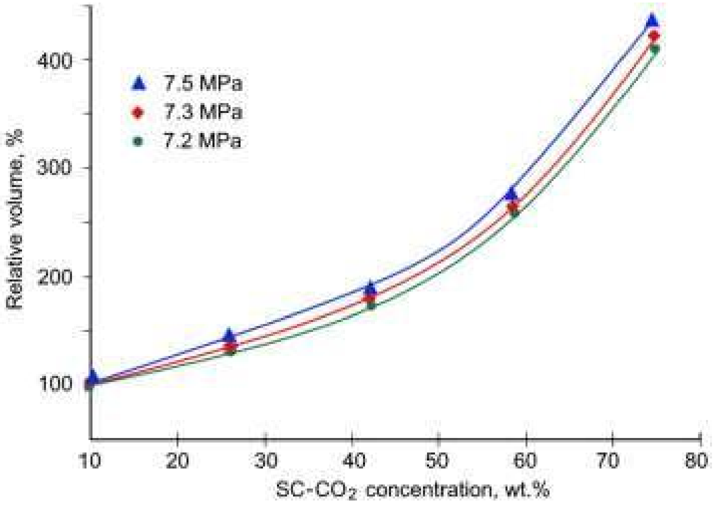


Figure 5. Dependence of the ratios of the volumes of oil mixtures on the concentration of sc-CO_2 at 303 K.

With an increase in the concentration of sc-CO_2 from 10 to 75 wt.%, the ratio of the volumes of mixtures to the volumes of the original oil increases by approximately 300% at a pressure of 7.5 MPa. The ratio of the volumes of mixtures to the volumes of the original oil weakly depends on pressure at low concentrations of sc-CO_2. With increasing concentration of sc-CO_2 in the mixture, this dependence intensifies.

At a concentration of sc-CO_2 of 10 wt.%, the volume of oil increases by 0.3% at a pressure of 15 MPa. A significant increase in volume occurs at an sc-CO_2 concentration of 23 wt.%. This is explained by the maximum saturation of oil with sc-CO_2 fluid and minimal recovery of light oil components. As the concentration of sc-CO_2 increases, the volume of extracted components exceeds the volume of sc-CO_2 saturating the oil. In this regard, the volume of the oil-containing phase is significantly reduced. The increase in the volume of the "heavy oil– sc-CO_2" system in the two-phase region occurs due to an increase in the volume of the light phase. In this case, the heavy phase decreases in volume due to the extraction of its components.

The distribution of the system volume relative to the volume of the original oil at 7.2 MPa is shown in Fig. 6. The lines of two-phase equilibrium "heavy phase" and "light phase" characterize the corresponding contributions of the phases to the increase in the volume of the system. By determining the thermobaric conditions for changes in the relative volumes of the phases occurring in the oil system, the boundaries for dividing the system mixture into two liquid phases: light CO_2 and heavy oil were established.

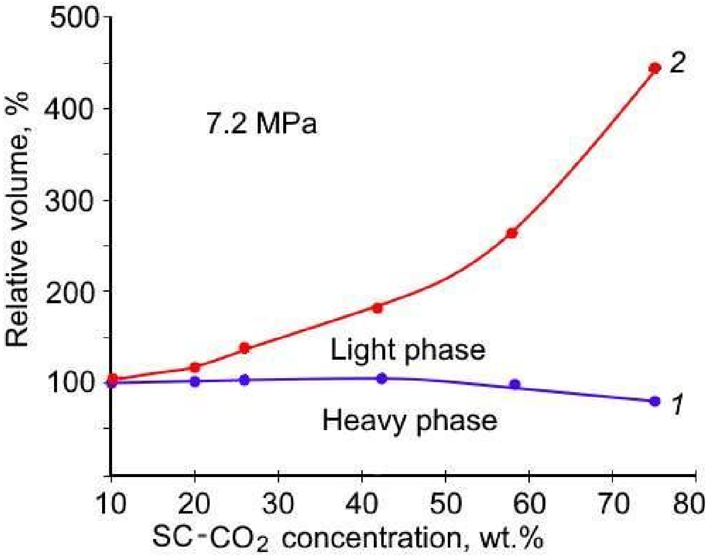


Figure 6. Dependence of the ratios of the volumes of oil mixtures on the concentration of sc-CO_2 in the “heavy oil– sc-CO_2” system at 303 K.

Light components of the oil system are intensively extracted already at a concentration of sc-CO_2 of 20 wt.%. In this case, relative to the total volume of the oil system, the volume of the heavy phase decreases slightly with an increase in the concentration of sc-CO_2 from 10 to 75 wt.% (Fig. 6). Thus, the concentration of sc-CO_2 20 wt.% in the “heavy oil– sc-CO_2” system is optimal, at which heat and mass transfer processes between phases lead to swelling of oil. In such a system, which does not contain a volumetric heat source, heat transfer can be described by the heat convection-diffusion equation [17]

$$\frac{\partial(c_pT)}{\partial t} = -\nabla(c_f\rho_f\nu_fT) + \nabla(D\nabla T) \quad (1)$$

where c_p is the specific heat capacity, t is the time, ρ is the density, ν_f is the kinematic viscosity of the fluid phase, D is the heat diffusion tensor of the corresponding component of the system, T is the temperature.

The physicochemical properties of displaced oil and displacement fluid are of practical importance for processing and characterizing a formation containing heavy oil. The isobaric dependence of the viscosity of the heavy phase of the system on the concentration of CO_2 is shown in Fig. 7.

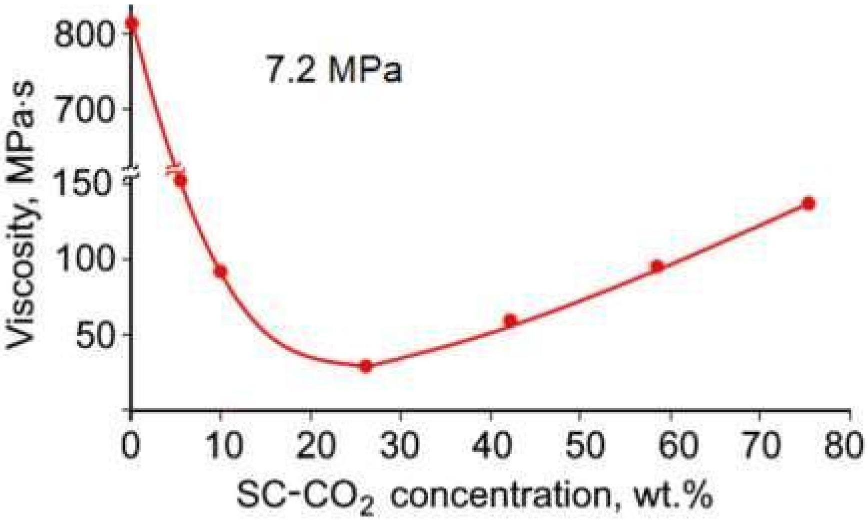


Figure 7. Isobaric dependence of the viscosity of the heavy phase of the system on the concentration of sc-CO_2 at 303 K.

Thus, studies of the influence of sc-CO_2 flow on oil recovery in the "heavy oil– sc-CO_2" system, including a porous medium in reservoir conditions, showed the following. The pressure in the sc-CO_2 flow drops sharply from 7.5 MPa to 7.2 MPa after the sc-CO_2 passes through the pores of the reservoir model containing heavy oil. Oil begins to flow into large pores in the core that were previously occupied by CO_2. This phenomenon of fluid interaction with oil-bearing core results in the final distribution of CO_2 saturation in the core. In this case, the viscous forces (internal friction) in the system are directed tangentially to the contacting layers of the liquid of the system. Internal friction opposes the movement of these layers relative to each other. Thus, viscous forces slow down the movement of the light phase more quickly and accelerate the movement of the heavy phase more slowly. Increasing the viscous force increases oil recovery in system. At the same time, maintaining supercritical pressure (≥7.2 MPa) is an important condition for the dissolution of CO_2 in heavy oil and the formation of a favorable viscosity coefficient in the system. This means that high oil displacement efficiency is achieved by injecting sc-CO_2 through the pores of oil-containing samples at reservoir temperatures and pressures of ≥7.2 MPa.

3.2. Effect of sc-CO_2 injection pressure

The extraction results of oil samples by injecting sc-CO_2 into the "heavy oil– sc-CO_2" system under different experimental pressures are shown in Fig. 8. As can be seen, the oil recovery ratio (EOR) increases with the increase of sc-CO_2 injection pressure. In the early stage, EOR increases and the viscosity of heavy oil decreases. At the critical pressure (7.5 MPa), the increase in EOR decreases as the sc-CO_2 injection pressure increases. The minimum mixing pressure of the sc-CO_2-heavy oil system is about 7.5 MPa at 303 K.

The sc-CO_2 pressure from the surface of heavy oil into the heavy oil– sc-CO_2system decreases due to the low permeability of the oil. Therefore, during the sc-CO_2 injection process, the injection pressure should be higher than 7.5 MPa. This pressure should be maintained to maximize the oil recovery during the sc-CO_2 injection period.

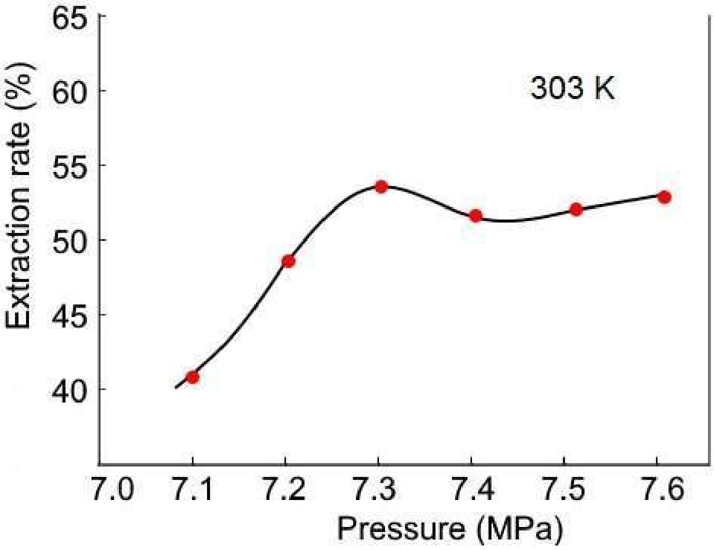


Figure 8. Dependence of oil recovery rate on sc-CO_2 injection pressure in the heavy oil–sc-CO_2 system.

3.3. Displacement of oil

The coefficient of oil displacement by sc-CO_2 in the "heavy oil– sc-CO_2" system was determined by the following method. The procedure for determining the oil displacement factor sc-CO_2 in laboratory conditions was as follows Fig. 2. An extractor 5 and a separator 6 made of corrosion-resistant steel were used, which made it possible to simulate a laboratory model of an oil reservoir. In extractor 5 the specified pressure and temperature values were maintained. The solvent mixture enters separator 6, where thermobaric conditions are also maintained.

This measuring setup ensured the supply of sc-CO_2 to the sample at reservoir pressure and a given constant carbon dioxide flow rate. The specified test temperature was maintained by a thermostat with an accuracy of ±1 K. The pressure drop across a fixed sample section was measured with a differential pressure gauge. Cuffs made of heat-resistant rubber were used as the insulating shell of the measuring setup. The model oil was stored in sealed, light-proof containers at room temperature for a series of experiments. Oil viscosity was determined at room and reservoir temperatures. To determine the extrusion coefficient, a rock sample was used, collected from individual cylindrical samples with an undisturbed structure, with a diameter of at least 25 mm. The temperature in the sample and oil containers was raised to the test temperature and maintained at the test temperature and pressure for at least 2 h.

Oil extraction parameters for each oil-saturated core sample are set individually. Reducing the extraction temperature below 304.3 K leads to a violation of the critical state of carbon dioxide and a decrease in the rate of extraction of the target product. The solvent pressure in the extractor should not be below 7.2 MPa, since in this case the solubility of sc-CO_2 sharply decreases.

Thus, the oil displacement experiment was carried out by introducing sc-CO_2 into an oil-containing measuring setup. To ensure the accuracy of the oil displacement results, a series of repeated experiments were carried out. In the experiments, the rate of heat exchange (heat charging/discharging) was determined from the temperature spread between the input and output temperatures $T_{\mathrm{f,in}}$ and $T_{\mathrm{f,out}}$, the volumetric heat capacity of the coolant sc-CO_2 $c_{\mathrm{f}}\rho_{\mathrm{f}}$ and its flow rate q_{f} according to equation (2)

$$Q_{\mathrm{c/d}} = c_{\mathrm{f}}\rho_{\mathrm{f}}q_{\mathrm{f}}\left(T_{\mathrm{f,in}} - T_{\mathrm{f,out}}\right). \quad (2)$$

Increasing the inlet temperature $T_{\mathrm{f,in}}$, can increase the rate of interaction of the components in the heavy oil- sc-CO_2 system. However, both the fluid flow rate q_{f} and $T_{\mathrm{f,in}}$, and the requirements for low $T_{\mathrm{f,out}}$ fluid will be determined by the specific conditions of application of sc-CO_2 and the composition of the oil.

The oil recovery factor is determined by the following relationship:

$$\eta = V_{\mathrm{ext}}/V, \quad (3)$$

where V_{ext} is the volume of displaced oil; V is the volume of oil in the reservoir before displacement begins.

The calculation deviation is determined by the equation

$$\delta_i = (V_{\mathrm{ext}} - V)/V \times 100\%. \quad (4)$$

The average deviation of the calculation is determined by the formula

$$\delta_{\mathrm{mean}} = \textstyle\sum_1^N |\delta_i|/N. \quad (5)$$

where *N* is the number of calculation points. For five series of experiments, the mean calculation deviation was δ_{mean} = 2.11%. Taking this into account, the time dependence of oil recovery was approximated by a continuous curve.

In Fig. 9 shows the time dependence of oil recovery during a single displacement of oil by sc-CO_2 fluid.

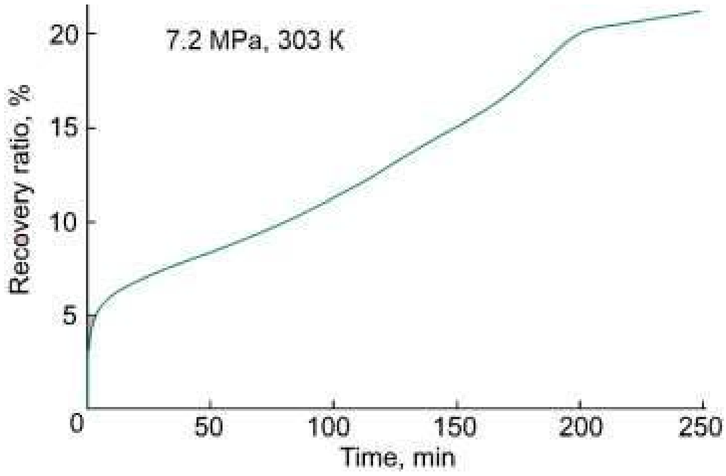


Figure 9. Time dependence of oil displacement during a single exposure of the oil system to the sc-CO_2 fluid at 7.2 MPa and 303 K.

Treatment of the oil system with sc-CO_2 fluid showed the following. When injecting sc-CO_2 with 10–15 wt.% in the system, the degree of oil recovery was low and amounted to about 8% in 10 min. When injecting sc-CO_2 with a concentration of 20 wt.%, oil recovery increases and amounted to 11% during this time. With an increase in the interaction time of sc-CO_2 with oil in the range of 50–200 min, the degree of oil recovery increases.

In conclusion, we note the following. The results obtained using the heavy oil- sc-CO_2 model for the binary system presented here indicate the following. Varying the thermobaric conditions of such a model can provide answers to questions of practical interest related to the critical lines in the phase diagram and maintaining equilibrium in the two-phase zone of the system. It is shown that the oil system under consideration can be unstable when interacting with sc-CO_2. This means that different initial conditions of the sc-CO_2 concentration, taking into account the critical point, can lead to different distributions of the sc-CO_2 concentration in the steady state in the system. For the specific problem of heavy oil displacement raised here, two cases can be defined by the initial sc-CO_2 concentration near the critical point. a) When the initial sc-CO_2 concentration is below the critical value (which depends on the composition of the oil), significant displacement of oil will occur in the region of the light phase. b) When the initial sc-CO_2 concentration is greater than the critical value, the interaction of the liquid with heavy oil will not cause significant displacement of oil. This conclusion does not seem to apply to extra-heavy oils as similar environments for interaction with sc-CO_2, although the oil recovery of such high-viscosity oils at sc-CO_2 saturation can be relatively high, since the ability of heavy oils to retain CO_2 is noticeable. The solution of this problem may provide some guidance on the correct choice of initial conditions for sc-CO_2 concentration and high-viscosity oils to ensure effective equilibrium maintenance and displacement of hard-to-recover oils.

The novelty of this work is that data on new aspects of oil displacement in the “heavy oil– sc-CO_2” model system have been obtained. The obtained data on *PVT* characteristics, the dependence of the phase volume distribution (light and heavy phases of the system) on the sc-CO_2 concentration may differ depending on the influence of thermodynamic characteristics and oil composition. Recovery of heavy oil with a noticeable recovery factor by conventional methods is a problem. The data we obtained allowed us to evaluate new properties on the critical lines of heavy oil systems containing sc-CO_2 near the critical point of the fluid. Taking this into account, the conditions for displacement of heavy oil and the recovery factor for hard-to-recover oils over time in the "heavy oil– sc-CO_2" model system have been determined. In particular, with a single exposure of such an oil system to sc-CO_2 (20 wt.%) at 7.2 MPa and 303 K for 200–250 min, the extraction coefficient averages 23%.

Thus, the method we used to study the heavy oil- sc-CO_2 system is a promising technology for efficient oil and gas recovery from hard-to-recover formations. As follows from the data obtained, like active water, CO_2 has the potential to develop hard-to-recover formations. The results of studying the effect of sc-CO_2 injection into heavy oil with the determination of oil recovery and oil displacement obtained over the past five years (see, for example, [17-25]) indicate that the "heavy oil– sc-CO_2" system requires further study. Diffusion-mass transfer sc-CO_2 can mobilize crude oil in both large and small pores and further increase oil recovery. The additional oil recovery of active sc-CO_2 after 4 injection cycles can be more than 25%. Due to its good diffusion and mass transfer ability, CO_2 can more fully participate in the oil displacement mechanism and further enhance oil recovery. The results of this paper can provide theoretical and experimental data to support the application of sc-CO_2 technology in tight reservoirs.

4. Nonequilibrium effects

In oil-solvent systems, as follows from the above, the study of nonequilibrium effects in oil solubility is important. However, the study of these phenomena requires separate consideration. Here we will present only the main patterns of using non-equilibrium effects important for studying oil-solvent systems (sc-CO_2). The interaction between oil components and solvents changes the rheological and phase characteristics of the oil.

Nonequilibrium interaction of the reservoir pressure maintenance system with oil are associated with the problems of filtration, mass transfer, and heat and mass transfer. It occurs, for example, when oil is displaced by a displacing agent (water, gas, surfactant, SCF, etc.). Under nonequilibrium conditions, such phenomena as capillary forces, phase transitions, chemical reactivity, etc. are taken into account.

Below we list the formulas that describe these nonequilibrium phenomena.
1. General expression for entropy production (nonequilibrium thermodynamics):

$$\sigma = \sum_i J_i X_i \geq 0 \quad (6)$$

where σ is the entropy production density per unit volume (non-negative), J_i is the thermodynamic flow (mass, heat, substance, etc.), X_i is the corresponding thermodynamic force (pressure gradient, temperature, concentration, etc.).
Generalized flows and forces within the Onsager theory are related with a linear relation

$$J_i = \sum_j L_{ij} X_j \quad (7)$$

where L_{ij} are the Onsager coefficients, reflecting the relationship between flows and forces (table). These kinetic coefficients satisfy the Onsager symmetry: $L_{ij} = L_{ji}$.

Table 1. Examples of flows and forces

J_i	X_i
Heat flow, $\vec{q}$	$\nabla(1/T)$
Diffusion flow	$-\nabla(\mu_k/T)$
Mass flow in a porous medium	∇P (pressure gradient) $\nabla\vec{v}$ (strain rate tensor)

Let us write down the basic equations used in the nonequilibrium displacement model.

1. Equation of non-stationary filtration of a two-phase fluid (oil + water):

$$\frac{\partial}{\partial t}(\phi S_w \rho_w) + \nabla\cdot(\rho_w \vec{v}_w) = q_w \quad (8)$$

$$\frac{\partial}{\partial t}(\phi S_n \rho_n) + \nabla\cdot(\rho_n \vec{v}_n) = q_n \quad (8a)$$

where ϕ is the porosity, S_w, S_n are the saturations with water and oil, $\rho_w \rho_n$ are the densities of water and oil, $\vec{v}_w, \vec{v}_n$ are the filtration velocities of the phases, q_w, q_n are the sources/sinks of the phases. As is customary, ∇ (nabla) is a vector differential operator whose components are partial derivatives with respect to the coordinates. Effective porosity is usually ϕ_{ef} = 15%.

2. The Darcy equation, which is important in oil production, is related to mass transfer in a porous medium. For multiphase (water–oil–gas) filtration, the Darcy equation is used for each phase, where relative permeabilities$k_{r\alpha}$ are introduced, where $\alpha \in \{w, o, g\}$. This equation has the form

$$\vec{v}\cdot\alpha = -\frac{k\cdot k_{r\alpha}}{\mu_\alpha}(\nabla P_\alpha - \rho_\alpha g \nabla\cdot z) \quad (9)$$

where $\vec{v}$ is the average filtration rate (m), k is the absolute permeability of the porous medium or rock (m^2), $k_{r\alpha}$ is the relative permeability of the liquid phase, μ_α is the viscosity of the liquid phase (Pa s), ∇P_α is the pressure gradient.

3. The equation of mass transfer (continuity) in the reservoir can be written as

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\vec{v}) = q \quad (10)$$

where ρ is the density of the liquid, q is the source or sink of the mass (e.g., a well).

4. Accounting for nonequilibrium mass transfer (e.g., for surfactants, solvents, CO_2):

$$\frac{\partial C}{\partial t} + \vec{v} \cdot \nabla C = D\nabla^2 C + R(C) \quad (11)$$

where C is the concentration of the component (e.g., surfactant), D is the molecular diffusion coefficient, $R(C$ is the term describing the reaction or adsorption (may be nonequilibrium).

5. Nonequilibrium model of component transfer (e.g., dissolution of gas in oil):

$$\frac{\partial C_g}{\partial t} = k_m \left(C_{g,eq} - C_g\right) \quad (12)$$

where C_g is the actual concentration of gas in oil, $C_{g,eq}$ is the equilibrium concentration, k_m is the mass transfer coefficient (describes the rate of approaching equilibrium).

6. Energy transfer equation:

$$\rho c_p \frac{\partial T}{\partial t} + \rho c_p \vec{v} \cdot \nabla T = \nabla \cdot (\lambda \nabla T) + Q \quad (13)$$

where λ is the thermal conductivity, Q is the internal heat sources (e.g., chemical reaction, friction, etc.), T is the temperature, c_p is the specific heat capacity at constant pressure.

5. Environmental considerations

Water is a vital element for human well-being and ecological balance. The oil and gas industry relies heavily on water at various stages of development, extraction and processing. They produce hazardous wastewater that is often discharged into the environment. The oil and gas industry also creates industrial waste that also pollutes the environment [26-30].

Traditional water treatment methods, particularly in the oil sector, consume a lot of water. We estimate that for example, to treat an oil well to extract 1 kg of heavy oil, about 100 liters of water solution are required. These methods introduce a number of toxic substances into the environment, such as salt, surfactants, metal ions and other chemicals. In addition, the energy and hot water required for well treatment are significant. Incomplete treatment of wastewater with poorly degradable chemicals from the industry leads to pollution of surface waters and contamination of aquifers. This also causes environmental damage and creates risks to public health and aggravates the environmental problem.

Water shortage and environmental pollution are becoming critical global issues. The oil industry, after agriculture and textiles, consumes a lot of water. Therefore, technology researchers are studying new and “clean” processes, which also leads to more solutions for environmental problems.

Sc-CO_2 has been used as a promising alternative to water to extract hard-to-recover oil. Field experiments have shown that sc-CO_2, with its low surface tension, high diffusion coefficient, low viscosity and high oil solubility, facilitates the extraction process (fig. 10).

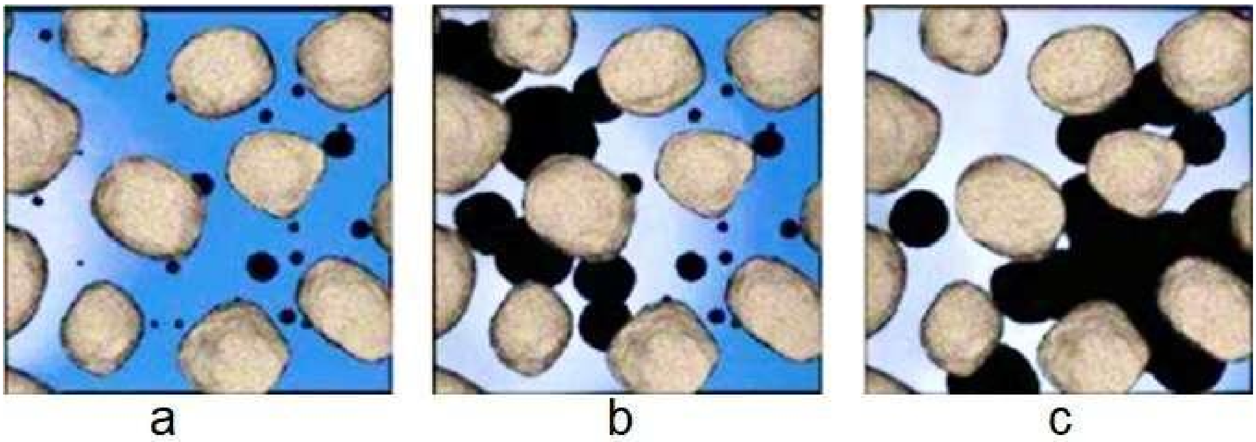


Figure 10. Scheme of swelling of oil particles during injection of CO_2 into a hard-to-recover oil formation. a – injected sc-CO_2 is trapped by oil in the reservoir, b – mix of sc-CO_2 and oil in the reservoir interact, c – oil expands in the sc-CO_2-oil mix and moves to the production well.

In this case, the oil reservoir processing time is also reduced. The temperature and pressure control allows the sc-CO_2 dissolving power to be adjusted. This results in high oil yields. Sc-CO_2 is known to be non-toxic, cost-effective, non-flammable and environmentally friendly. Sc-CO_2 oil processing does not require water or chemicals, which reduces wastewater.

In addition, sc-CO_2 processing uses CO_2 as a by-product of industrial processes. This reduces the impact of CO_2 on the environment. The sc-CO_2 can be recovered, recycled and reused, minimizing the contribution of CO_2 to the greenhouse effect.

Thus, the stages of development, extraction, refining and processing of oil use water and produce hazardous wastewater. Whereas, clean water is necessary for both human well-being and the ecosystem. In other words, the processes of the oil industry contribute to environmental pollution. At the same time, they create various toxic wastes and use significant amounts of non-renewable resources and energy.

On the contrary, the process of processing hard-to-recover oil sc-CO_2 increases the environmental friendliness and efficiency of extraction. Processing of oil sc-CO_2, in particular, ensures the efficient extraction of high-viscosity oils with high yield. As noted above, the solvent is non-toxic, cost-effective, does not create waste and environmental problems.

6. Economic considerations

Adaptation of sc-CO_2 processing to industrial conditions faces a challenge due to high initial investment costs. This is due to the construction of expensive installations for oil production and processing using sc-CO_2. However, using the initial installation and operating costs, there is promise for high results leading to environmentally friendly products and production processes [26-30].

Sc-CO_2 treatment of an oil well reduces operating costs (by 20%) compared to traditional methods using water. At the same time, energy consumption and well treatment time are reduced. For example, for one well, the treatment time is halved compared to 4 hours with traditional methods. CO_2 is released in a gaseous state. This saves energy. sc-CO_2 treatment reduces costs associated with water intake and wastewater treatment.

Our laboratory and field (Siyazan field) studies have shown that the operating costs of oil production using sc-CO_2 are from 0.8 to 1.1 US dollars per kilogram of oil. This is significantly lower than using water treatment methods. The reduction in costs using sc-CO_2 is due to the exclusion of auxiliary substances (e.g. surfactants, dispersants) for treating oil wells. In addition, sc-CO_2 treatment significantly reduces the loss (~1%) of recoverable heavy oil compared to water well treatment methods. At the same well treatment temperature and a decrease in the treatment pressure near the critical point of CO_2 (7.2 MPa), energy consumption decreased from 200 kW h to 180 kW h. Control of the parameters of the sc-CO2 treatment process allows optimizing the energy efficiency and cost effectiveness of the viscous oil recovery process. Liquid sc-CO_2 units are mobile and can be installed in a convenient location near the well. This reduces transportation costs and simplifies product extraction compared to water-based units, which must be located in areas with access to water.

Using sc-CO_2 solvent as an oil recovery medium is an environmentally friendly process. CO_2 gas is non-toxic and non-flammable, and all sc-CO_2 oil well treatment cycles do not require the use of water. Sc-CO_2 oil recovery does not use chemicals. The sc-CO_2 well treatment process does not involve direct interaction with people or animals during the testing and execution stages. This ensures the safety of the sc-CO_2 oil well treatment process.

The results of these studies demonstrate the effectiveness of using sc-CO_2 to recover heavy oil. This method saves significant amounts of water, reduces energy consumption and eliminates wastewater generation. In addition, the simple operation of sc-CO_2 injection equipment requires minimal personnel involvement. This reduces the risk of exposure to hazardous chemicals, thereby providing an environmentally friendly approach to oil recovery.

7. Conclusions

1. A study of the effect of various parameters (temperature, pressure and time) on the oil recovery rate using sc-CO_2 as a dissolving medium showed the following. The optimum treatment parameters are 32 °C, 7.2 MPa and 1 h, compared to the standard parameters of wet water treatment of an oil well. These treatment conditions increase the oil recovery rate and the stability of the process. Studies of the patterns of volumetric and phase behavior of heavy oil when interacting with SC-CO_2 at reservoir temperatures and pressures have shown the following. In the “heavy oil–SC-CO_2” system, the conditions for changing *PVT* properties of fluids when fluid is pumped into the system are determined.

2. The conditions for changing PVT characteristics when injecting fluid into the heavy oil-SCF CO_2 system significantly affect the degree of oil recovery. The volume of the heavy phase relative to the volume of the system decreases linearly with increasing concentration of SC-CO_2 in contact with it. The SC-CO_2 concentration of 20 wt.% allows for maximum oil swelling. Increasing the pressure (above 7.5 MPa) of SC-CO_2 injection into the “heavy oil – SC-CO_2” system leads to an increase in the oil recovery factor. A further increase in the SC-CO_2 injection pressure does not significantly affect the oil recovery

factor. High SC-CO_2 injection pressure accelerates mass exchange between CO_2 molecules and heavy oil, which is associated with the high solubility of the components in each other.

3. The effect of sc-CO_2 flows on oil recovery in the "heavy oil– sc-CO_2" system sharply reduces the pressure from 7.5 MPa to 7.2 MPa. Viscous forces and oil recovery increase above the pressure 7.2 MPa. Thus, oil displacement through the pores of oil-containing samples in the reservoir model is intensified at reservoir temperatures and pressures. The obtained results of reservoir processing on isobars from 7.2 to 7.5 MPa for heavy oil can be used in the design of oilfield equipment. This is important for the development of high-viscosity hydrocarbon deposits.

4. Oil recovery was determined using created reservoir models that reflect the process of oil displacement. Fluid treatment of the oil reservoir was also carried out at a depleted oil well in the Siyazan field. Optimal adjustment of PVT parameters ensures high oil recovery in the heavy oil-fluid system. In addition, under optimized conditions of oil reservoir processing, the rate of extraction of resinous substances from heavy oil is also maximum. When pumping sc-CO_2 into a system with heavy oil, the oil displacement time is significantly reduced. The flow rate and degree of oil displacement increase. The average degree of heavy oil recovery when pumping sc-CO_2 increases by 23% in 120 min. compared to treating the well with water. Environmental and economic considerations for the use of CO_2 fluid are proposed.

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Conflict of interest

The authors declare that they have no conflict of interest.

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