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10.00 – 12.30 Session 1 – Environment – Climate Change - Energy
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10.30 – 10.50

Prof. Rauf ALIYAROV

Assoc. Prof. Salim ASADOV (on line)

**“Geotechnological Problems of Oil, Gas and Chemistry” Scientific
Research Institute, Azerbaijan**

**“Application of SCF CO₂ to enhance oil recovery from
reservoirs in a non-equilibrium state”**

E.N. Aliev, Salim M. Asadov, H. Kh. Malikov, R.Yu. Aliyarov

**Application of SCF CO₂ to enhance oil recovery from reservoirs
in a non-equilibrium state**

**Scientific Research Institute Geotechnological Problems of
Oil, Gas and Chemistry. Azerbaijan State Oil and Industry
University. 20 Azadlig Ave., Baku, AZ-1010 Azerbaijan
e-mail: r.aliyarov@asoiu.edu.az; h.malikov@gpogc.az**

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-CO₂) displacement technology can be used in a wide range of thermobaric and physicochemical conditions in the reservoir.

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.

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 CO₂. 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-CO₂.

The *PVT* installation diagram is shown in Fig. 1. A mixture of formation oil and sc-CO₂ was placed in pump cell 1. Sc-CO₂ was pumped into auxiliary cell 2. Mixing of the components of the “heavy oil–sc-CO₂” 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.

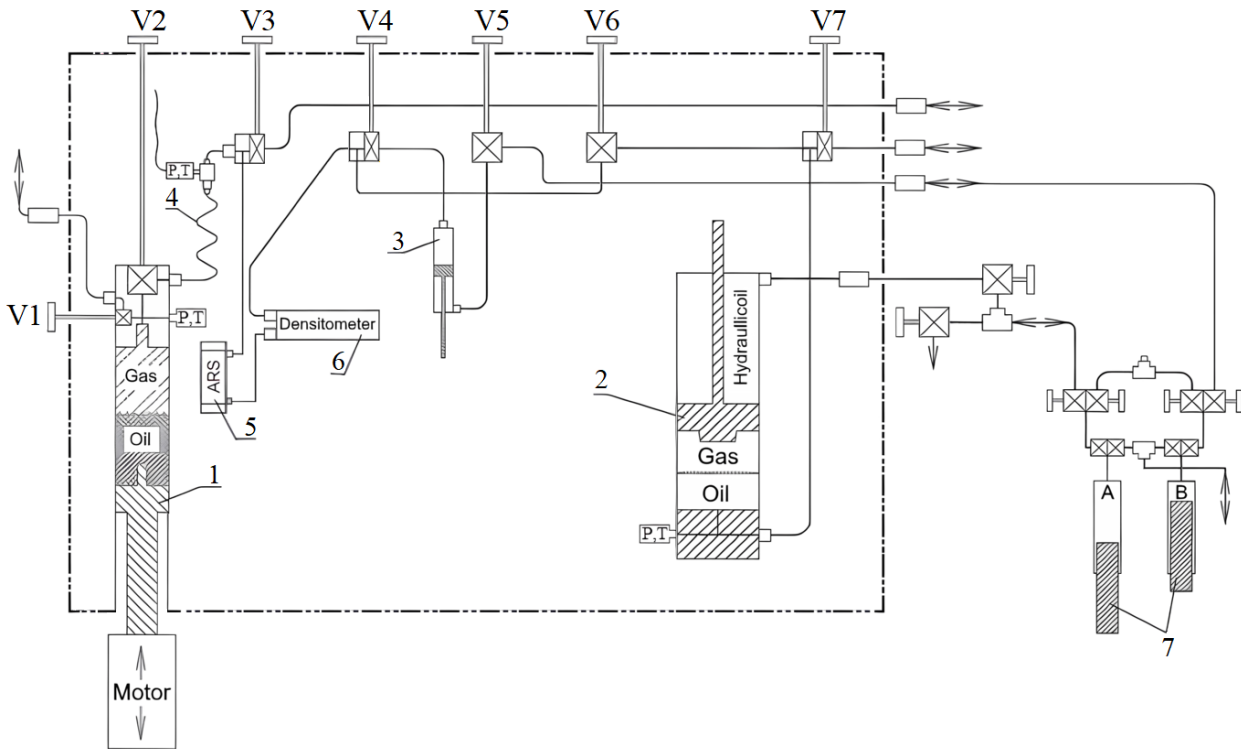


Fig. 1. Installation diagram of *PVT* 3000-L:

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-CO₂ fluid was changed in the range of 10–30 wt.%. At a concentration of sc-CO₂ 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-CO₂ 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.

CO₂ 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-CO₂ is pumped into the pipeline of the unit simulating a model of the system of hard-to-recover heavy oil containing sc-CO₂. In such a system, the CO₂ remained in the form of a supercritical fluid.

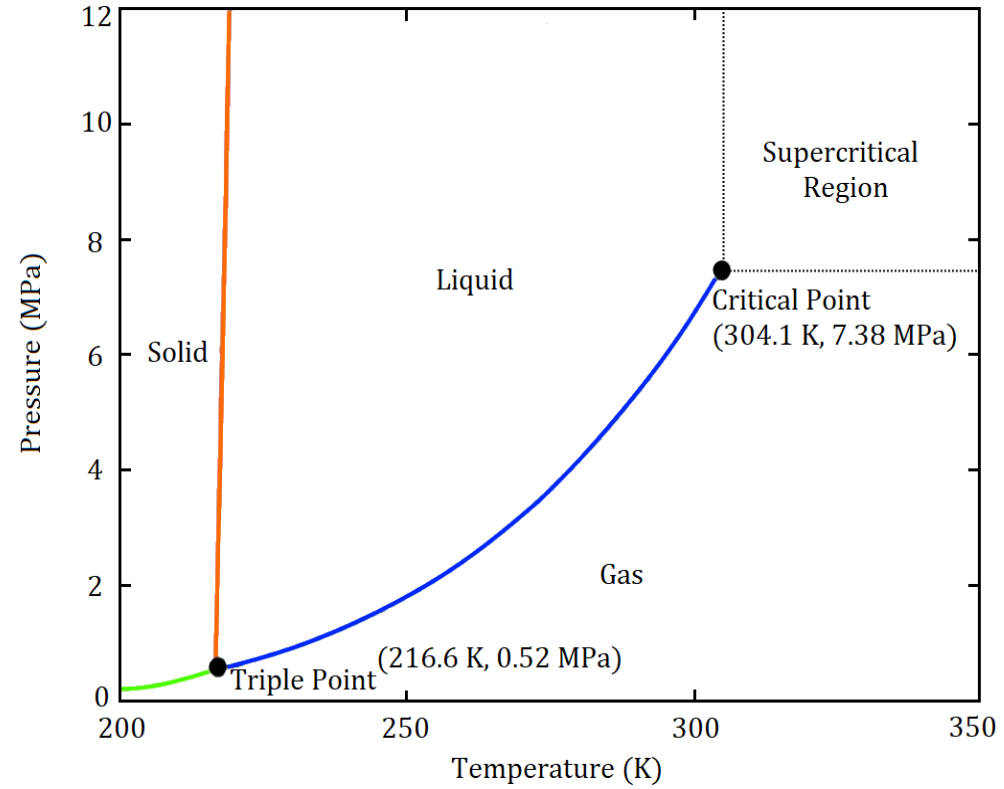


Fig. 3. Phase diagram of CO₂.

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-CO₂” systems. The patterns of changes in the volumetric and phase behavior of high-viscosity oil when interacting with sc-CO₂ have not been systematically studied previously.

3.1. PVT Properties of Fluids

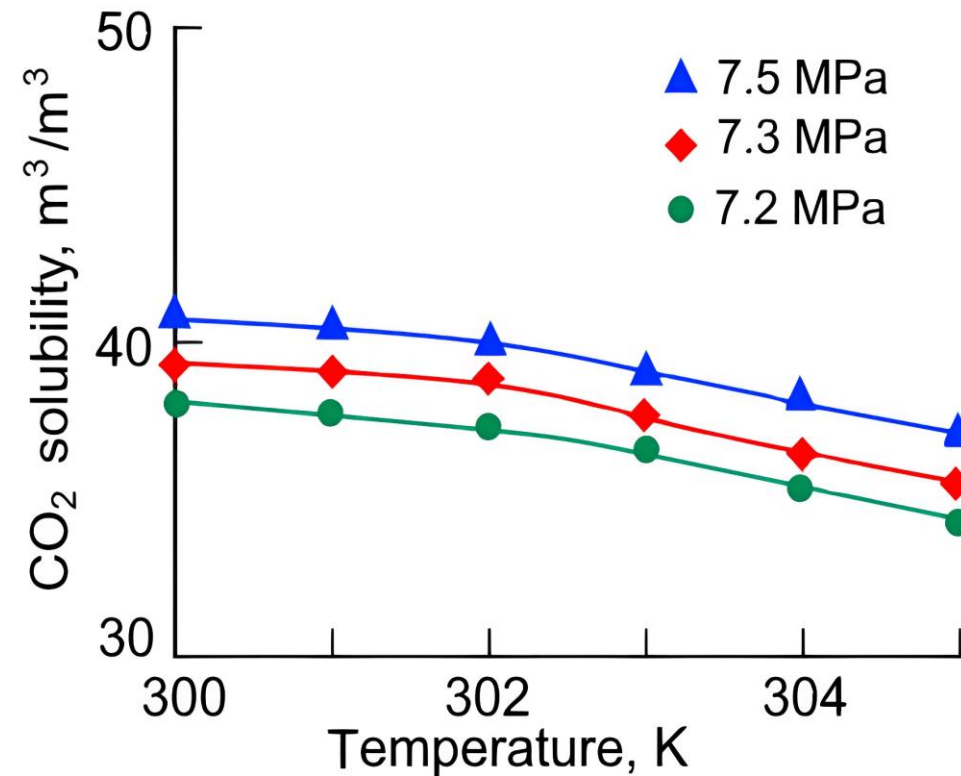


Fig. 4. Dependence of CO₂ solubility on temperature at 7.2–7.5 MPa in heavy oil.

The dependence of the ratios of the volumes of oil mixtures on the concentration of sc-CO₂ (10-75 wt.%) at 7.2–7.5 MPa and 303 K is shown in Fig. 5.

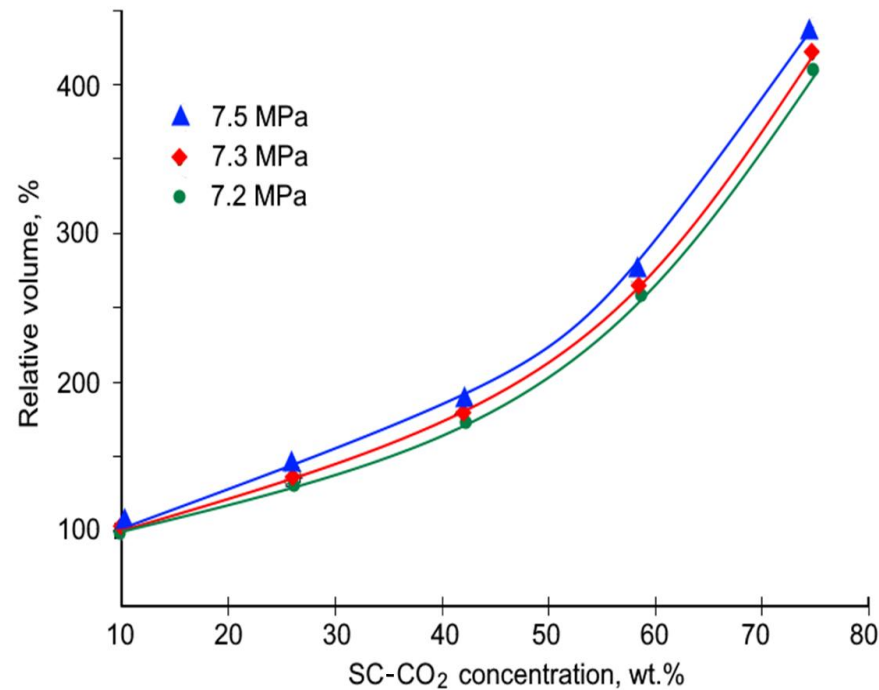


Fig. 5. Dependence of the ratios of the volumes of oil mixtures on the concentration of sc-CO₂ at 303 K.

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 CO₂ and heavy oil were established.

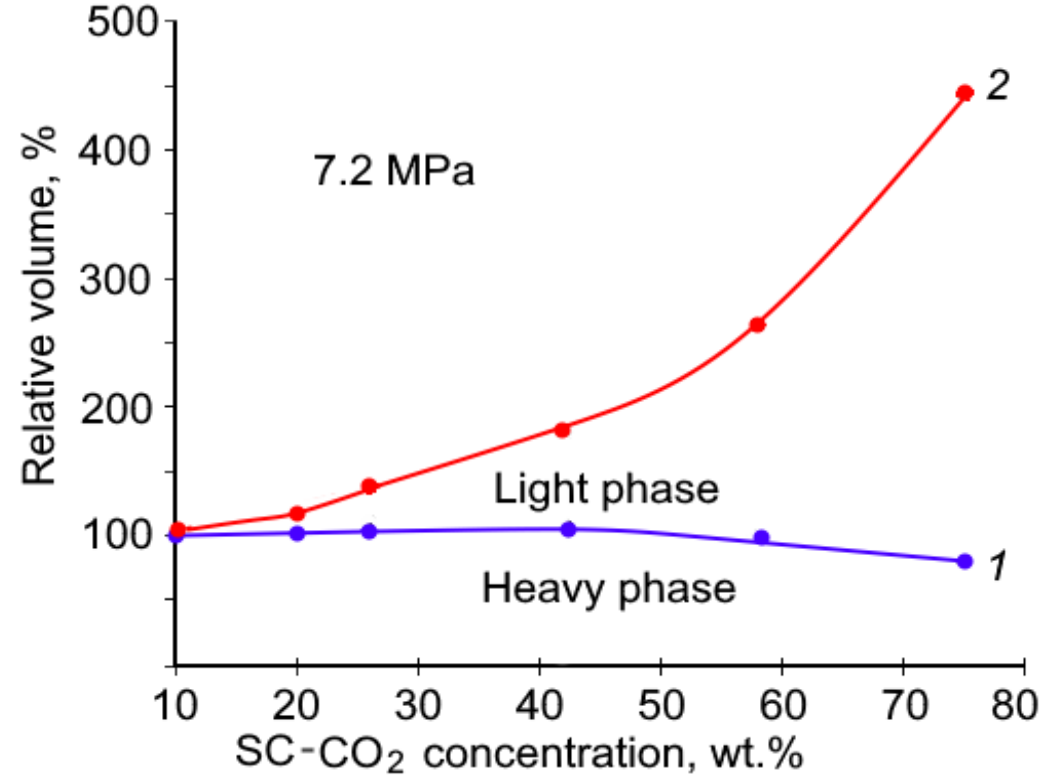


Fig. 6. Dependence of the ratios of the volumes of oil mixtures on the concentration of sc-CO₂ in the “heavy oil–sc-CO₂” system at 303 K.

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 CO₂ is shown in Fig. 7.

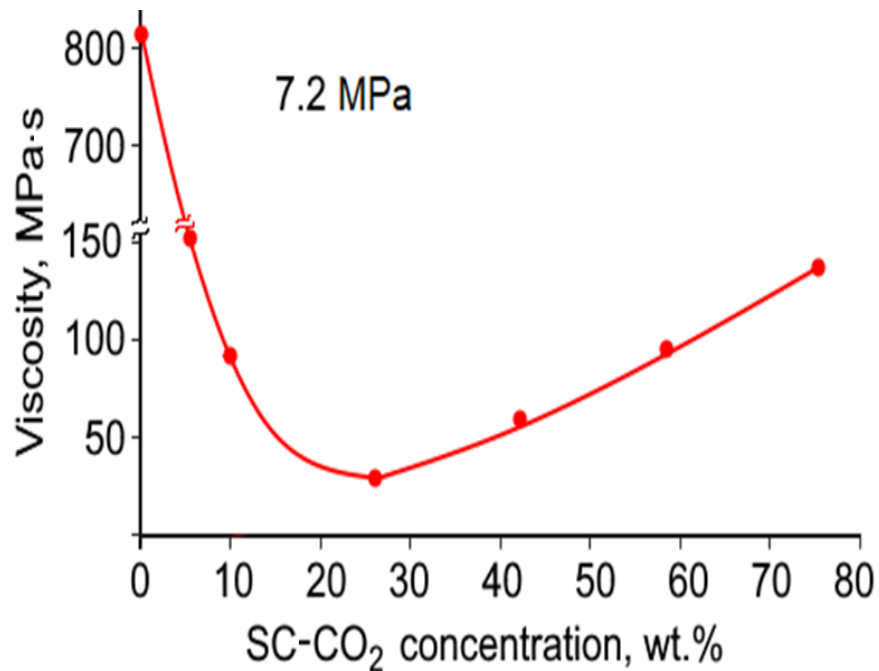


Fig. 7. Isobaric dependence of the viscosity of the heavy phase of the system on the concentration of sc-CO₂ at 303 K.

3.2. Effect of sc-CO₂ injection pressure

The extraction results of oil samples by injecting sc-CO₂ into the “heavy oil– sc-CO₂” 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-CO₂ 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-CO₂ injection pressure increases. The minimum mixing pressure of the sc-CO₂-heavy oil system is about 7.5 MPa at 303 K.

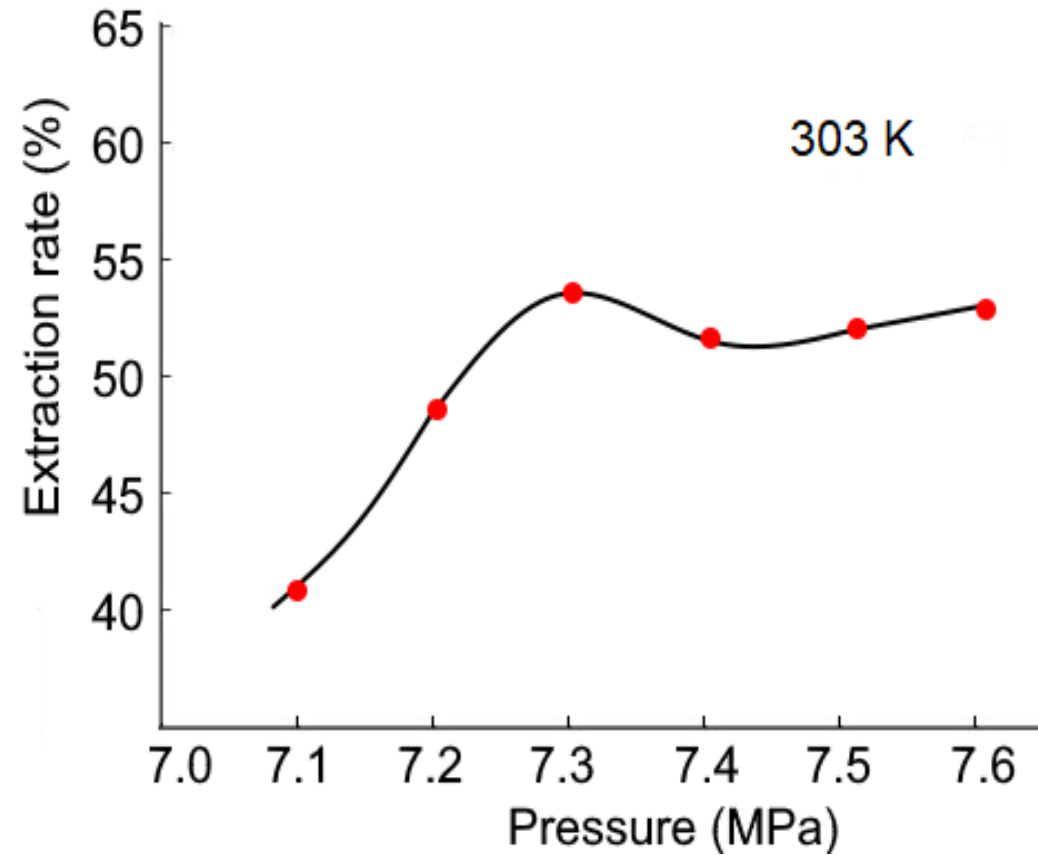


Fig. 8. Dependence of oil recovery rate on sc-CO₂ injection pressure in the heavy oil–sc-CO₂ system.

In Fig. 9 shows the time dependence of oil recovery during a single displacement of oil by sc-CO₂ fluid.

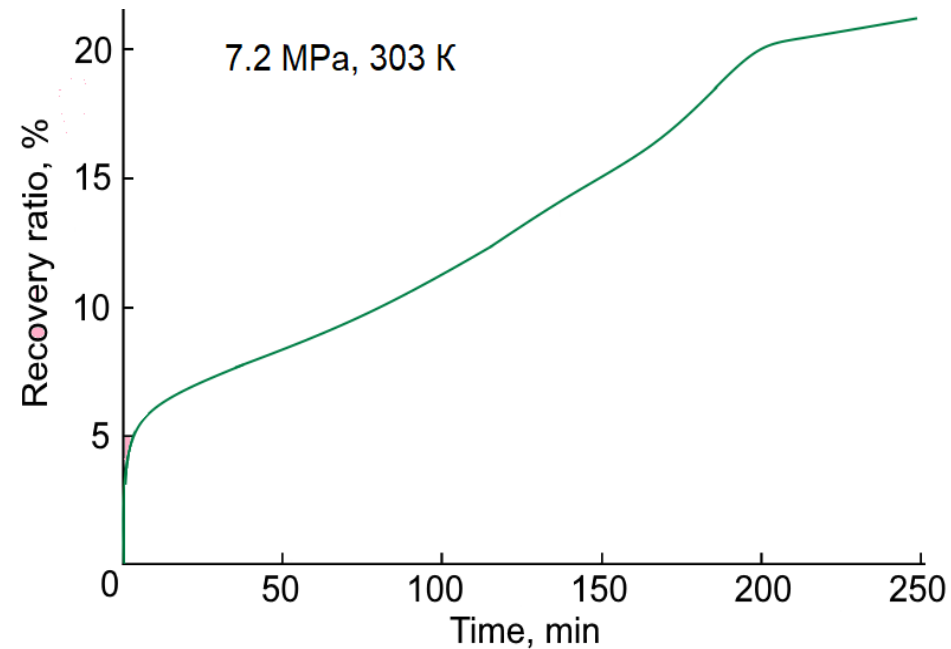


Fig. 9. Time dependence of oil displacement during a single exposure of the oil system to the sc-CO₂ fluid at 7.2 MPa and 303 K.

4. Nonequilibrium effects

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

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

5. Environmental considerations

Sc-CO₂ has been used as a promising alternative to water to extract hard-to-recover oil. Field experiments have shown that sc-CO₂, with its low surface tension, high diffusion coefficient, low viscosity and high oil solubility, facilitates the extraction process (fig. 10).

Processing of oil sc-CO₂, 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.

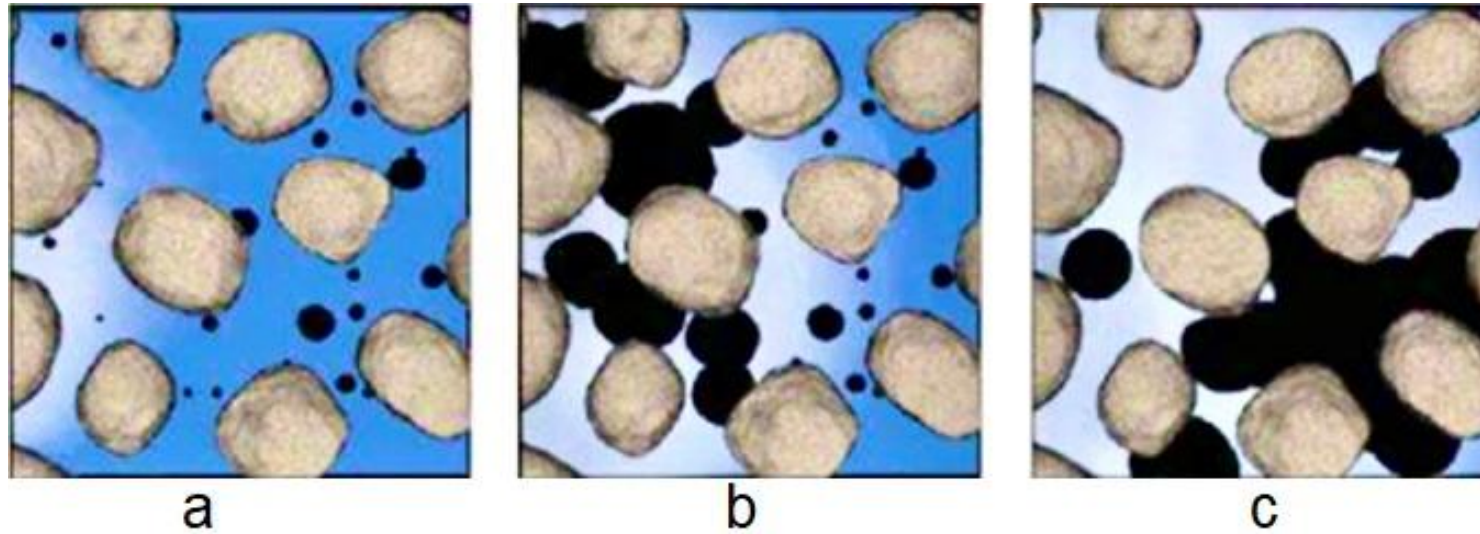


Fig. 10. Scheme of swelling of oil particles during injection of CO₂ into a hard-to-recover oil formation. a – injected sc-CO₂ is trapped by oil in the reservoir, b – mix of sc-CO₂ and oil in the reservoir interact, c – oil expands in the sc-CO₂-oil mix and moves to the production well.

6. Economic considerations

Sc-CO₂ 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. CO₂ is released in a gaseous state. This saves energy. sc-CO₂ treatment reduces costs associated with water intake and wastewater treatment.

The reduction in costs using sc-CO₂ is due to the exclusion of auxiliary substances (e.g. surfactants, dispersants) for treating oil wells. In addition, sc-CO₂ treatment significantly reduces the loss (~1%) of recoverable heavy oil compared to water well treatment methods.

The results of these studies demonstrate the effectiveness of using sc-CO₂ 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-CO₂ 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-CO₂ 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-CO₂ at reservoir temperatures and pressures have shown the following. In the “heavy oil–SC-CO₂” 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 CO₂ 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-CO₂ in contact with it. The SC-CO₂ concentration of 20 wt.% allows for maximum oil swelling. Increasing the pressure (above 7.5 MPa) of SC-CO₂ injection into the “heavy oil – SC-CO₂” system leads to an increase in the oil recovery factor. A further increase in the SC-CO₂ injection pressure does not significantly affect the oil recovery factor. High SC-CO₂ injection pressure accelerates mass exchange between CO₂ molecules and heavy oil, which is associated with the high solubility of the components in each other.

3. The effect of sc-CO₂ flows on oil recovery in the "heavy oil–sc-CO₂" 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-CO₂ 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-CO₂ increases by 23% in 120 min. compared to treating the well with water. Environmental and economic considerations for the use of CO₂ fluid are proposed.

Thank you for your attention!

