Study of adsorption and desorption of asphaltene sediments inhibitor in the bottomhole formation zone

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Abstract
Background: Studies of asphaltene sediments (AS) formation in microvolume of reservoir voids were carried out. It was found for test oil that paraffin saturation point in microvolume is higher by 6-9°C than in free volume. Early transition of paraffins into solid phase leads to complications associated with formation of AS and reduces efficiency of physicochemical methods of prevention AS formation based on batching of inhibitor into bottomhole.

Methods: For prevention of AS formation in oil reservoir usage of bottomhole formation zone (BFZ) as a natural batcher of AS inhibitor into oil was proposed by authors. Studies on adsorption of inhibitor on rock walls during its injection into formation and subsequent desorption during elution of inhibitor from reservoir of produced oil were conducted. Findings: Analysis of experimental results allowed to define effective concentration of AS inhibitor in oil during injection of inhibitor into BFZ, time of inhibitor adsorption on rock walls, as well as duration of inhibitor desorption from reservoir. Improvements: It was found that injection of AS inhibitor solution into BFZ will reduce paraffin saturation point in reservoir pore space.

Keywords: Asphaltene Sediments, Asphaltene, Resins, Paraffins, Paraffin Saturation Point.

INTRODUCTION
For the moment development of oil fields in Russian Federation is accompanied by quality reduction of extracted product, which is connected with increase of share of resources whose production is problematic as well as with transition of majority of producing fields to the final stage of development, accompanied by increase of water cut of oil reservoirs and increase of content of high-molecular oil components – asphaltenes, resins and paraffins and change in thermobaric conditions of reservoirs development [3]. Production of oil with high content of paraffins, asphaltenes and resins is complicated by AS formation on rock walls and wetted surfaces of downhole equipment [4]. Transition of high-molecular oil components into solid phase (AS formation) can take place not only in well, but also in pore space of oil reservoir, which in turn will lead to narrowing of pore channels and reduction of reservoir rocks permeability.

AS formation in "reservoir-well" system occurs during oil cooling below paraffin saturation point (temperature of paraffin crystallization), so this process starts with transition of paraffin from liquid to a solid crystalline state. It should be noted that phase transitions of paraffins in pore volume of oil reservoirs are poorly studied. Reportedly paraffin saturation point in microvolume is higher by several degrees than in free volume of oil [1, 2].
sedimentation at pressures up to 103 MPa and temperatures up to 170°C. It allows identifying solid particles and monitoring changes in size and morphology of resulting asphaltene particles as a function of temperature, pressure, time and influence of various reagents (CO₂, AS inhibitors, SAS, solvents, etc.).

2) Laser system of solid particles detection (SDS) is used for determination of sedimentation conditions of asphaltenes and paraffins in formation fluid.

3) HPHT filtration system is designed for measurement of solid particles amount in sample of fluid at different PVT conditions.

Oil samples were selected and prepared in accordance with instructions and recommendations of Vinci Technologies. Sample preparation included heating sample of oil up to 90°C in special loading device, which supply oil into PVT cell for testing. Heating of oil is required for complete dissolution of paraffins, asphaltenes and resins. After loading PVT cell is isolated with a special high pressure valve. Sample of oil is thermostated within 24 hours in PVT cell. Systems of SDS and HPM are commonly used to study the process of paraffin and asphaltenes sedimentation.

General methodology of experiments was as follows:
1. Setting of constant pressure in PVT cell (isobaric process). That pressure will be unchanged within any changes in system due to pump operation.
2. Gradual decrease of temperature by cooling PVT cell using temperature control system. System of constant stirring at a certain speed is included for simulation of oil flow in well. Data writing is carried out on a hard disk.
3. Analysis of obtained information in order to study conditions of asphaltenes substances sedimentation.

To determine conditions of paraffins and asphaltenes sedimentation isobaric method was selected in which pressure in the system is kept constant and temperature varies in given interval. Pressure in system was selected equal to 24 MPa on the basis of field data.

Filtration studies
Filtration studies were conducted on automated installation AutoFlood 700 to assess condition ratio in simulation of reservoir thermobaric conditions on natural samples of terrigenous rocks. Experiments were conducted in "constant flow rate – changeable pressure differences" mode. The main controllable parameter in experiments was change of pressure difference that determines change of fluids mobility and permeability of core sample.

Reservoir conditions of laboratory filtration experiments were:
1) Rock pressure of 38 MPa;
2) Pore (reservoir) pressure of 24 MPa;
3) Filtration rate (flow rate) of 0,5 cm³/min.

Filtration experiment was conducted by method comprising the following steps:
1) Prepared core sample was saturated under vacuum by prepared model of reservoir water. After saturation pore volume of core sample was determined by weighting according to change of its mass;
2) Saturated core sample was placed into core holder of filtration plant AutoFlood 700, where realistic temperature and pressure conditions were created close to reservoir ones;
3) Temperature in oven was set up by 10-15°C above paraffin saturation point in free volume;
4) Test oil was pumped through the core sample at constant flow (0,5 cm³/min), reducing temperature in core holder by one degree every 3 hours.

Basic information about study samples of oil and reservoir rock:
- Oil – light (density ~ 829 kg/m³), low viscosity (viscosity ~ 13,1 MPa·c), paraffin-base (paraffin ~ 7,8 % wt, asphaltenes ~ 1,8 % wt, resins ~ 3,5% wt);
- Rock – carbonate, an open porosity ~ 11%, permeability ~ 160·10⁻³ µm²

During research in function of AS inhibitor a reagent conventionally called GK-1(SAS) was used, which is a mixture of polar copolymers with vinyl acetate in hydrocarbon solvent (benzene). Choice of this reagent is justified by its high surface activity and presence of resins concentrate in its composition.

Experiment was conducted to determine paraffin saturation point in a free volume on installation designed for studying generation of solid substances in formation fluid (FLASS system of Vinci Technologies). Principle of method consists in sequential reduction of temperature (from 80°C to 20°C) of oil in PVT cell at constant pressure with continuous recording of sample state with help of microscopy under high pressure and subsequent processing by program particle size analysis. Results of conducted studies are shown in Figure 2.

![Figure 2. Dependence of amount of paraffin solid particles in oil from temperature](image-url)
For determination of paraffin saturation point in pore space of rock we used indirect ("filtration") method of its assessment based on experimental recording of dependence of filtration characteristic of oil-saturated rock from temperature. Oil was filtered through core sample at a constant flow (0.5 ml/min) with periodical temperature reduction in core holder (by one degree every three hours). Results of filtration study are shown in Figures 3 and 4.

**Figure 3.** Dynamics of change in pressure gradient of oil flow through core sample with periodic temperature reduction (from 43°C to 34°C)

![Figure 3.](image1)

**Figure 3.** Dependence of core sample permeability to oil from temperature (taking into account change of oil viscosity on temperature).

According to diagrams in Figures 3 and 4 it is apparent that at temperature of 39°C there is a sharp increase in pressure gradient of filtration and reduction of permeability to oil of core sample that can be explained by formation of solid paraffin particles in pore space.

Thus, results of experiments have allowed to establish that for test oil formation of solid paraffin particles in porous medium occurs at temperature up by 5-7°C higher than in free volume. This important practical result should be considered when dealing with complications associated with the formation AS. So, if crystallization of paraffin started as early as in reservoir, this process will also affect AS formation in well because stable nucleuses of solid phase will play role of crystallization centers for further formation of sediments, scaling up risk of complications in well.

As well if beginning of solid paraffin crystals formation occurs in reservoir, then question remains open about effectiveness of dosing of AS inhibitor into bottom hole, i.e. after beginning of paraffins phase transition [7]. To answer this question comparisons of dynamics of growth of paraffin crystals amount were carried out while inhibiting oil before formation of paraffin solid particles at 37°C (Figure 5.1.a) and oil inhibiting after phase transition of paraffin at temperature of 31°C (Figure 5.1.b).

**Figure 5.1.** Condition of oil sample at the moment of injection of AS inhibitor: a) temperature 37°C, b) temperature 31°C

Temperature of both samples was reduced after inhibiting by the same rate with constant recording of sample condition with the help of microscopy. Conditions of both samples at temperature of 24°C are shown in Figure 5.2.
Figure 5.2. Results of microscopy of oil samples at temperature of 24°C: a) injection of AS inhibitor was carried out at 37°C, b) injection of AS inhibitor was carried out at temperature of 31°C.

Results of the study showed that injection of AS inhibitor with depressor effect into produce of well will be effective during its supply before beginning of solid paraffin particles formation, therefore, supply of inhibitor into bottom hole in case when phase transition of paraffin already began in reservoir, will not be effective. In response to this problem it was proposed to inject AS inhibitor into bottomhole formation zone (BFZ) with subsequent adsorption of inhibitor on the rock and its gradual "washing out" during well operation.

During injection of AS inhibitor into BFZ it is necessary to be guided not only by inhibiting ability of reagent, but also by adsorption-desorption characteristics of inhibitor that affect adsorption of reagent on the rock and its subsequent desorption. At the same time it is known that formation rocks have different adsorbing ability. Therefore, requirements to AS inhibitor are strict: on one hand, it must be adsorbed on the rock surface during injection rather rapidly, firmly and as more as possible, and on the other hand, be desorbed as slowly as possible from this surface in the process of well operation [8], at that its concentration in produced oil must not be below allowed minimum (not lower than 0.01 % wt for test oil).

Studies of AS inhibitor considering its adsorption and desorption abilities will allow to give recommendations which provide minimum removal of reagent and increase effectiveness of prevention of AS formation. Processes of adsorption and desorption are affected by hydrodynamic conditions of fluids movements, composition and properties of rocks, time, concentration of inhibitor and other factors, effects of which are not fully studied.

Evaluation of adsorption kinetics of AS inhibitor was conducted in laboratory condition by filtration studies on FDES-645 installation (of Coretest Systems Corporation). The main element of the installation is core holder with the adsorbent. Core material was used as an adsorbent.

The first stage of laboratory study was saturation of core sample by oil. Then filtering of oil with specified content of AS inhibitor was carried out up to constant concentration of inhibitor in oil at inlet and outlet of core holder. For determination of inhibitor content in oil at outlet of core holder dependence was built of oil interfacial tension on the border with water from concentration of inhibitor in oil (Figure 6). At outlet of core holder sampling was periodically performed for evaluation of interfacial tension on the border with distilled water, by value of which mass content of inhibitor in oil was determined.

Figure 6. Dependence of oil interfacial tension on the border with distilled water from concentration of AS inhibitor in oil.

Figure 7. Dynamics of change of AS inhibitor concentration in oil at the outlet of core holder.
Results of study of AS inhibitor adsorption are shown in Figure 7. They show that adsorption equilibrium in core sample occurs after 26 hours of pumping 0.3% solution of inhibitor, 10 hours of pumping 0.5% solution of inhibitor, 8 hours of pumping 1% solution of inhibitor and 7 hours of pumping 2% solution of inhibitor.

For assessment of kinetics of inhibitor desorption through core samples, in which its adsorption took place, oil without reagent was pumped and at outlet of core holder concentration of inhibitor in oil was measured. Results of the study are presented in Figure 8.

Figure 8. Dependence of concentration of AS inhibitor in oil at outlet of core holder from volume of pumped solution.

Figure 8 shows results of study of inhibitor desorption dynamics depending on concentration of inhibitor in oil during injection into core sample. Results of the study show that after pumping 200 pore volumes of oil, desorption of reagent becomes constant regardless of initial concentration of inhibitor and until pumping 530-550 pore volumes concentration of inhibitor exceeds value of 0.01%. However, in case of injection of inhibited oil into formation with inhibitor content more than 0.5%, subsequent washing out of inhibitor occurs in amount which exceeds required content for effective protection against AS formation, which in turn negatively affects technical and economic assessment of action. In future, in case of injection 0.3% and 0.5% solution of inhibitor during its "washing out" from reservoir, early removal of inhibitor does not happen and its concentration remains sufficient for a long time for effective prevention AS formation in well.

Therefore, optimal concentration of AS inhibitor for injection into reservoir is 0.5% wt because of relatively high speed of adsorption of inhibitor on pore walls (Figure 7) and due to relatively small losses of reagent during its desorption (Figure 8).

As a check on effectiveness of preventing sediments formation in reservoir filtration experiment was conducted, essence of which consisted in pumping oil with AS inhibitor (0.5% wt) through carbonate core with a flow rate of 0.5 ml/min for 12 hours, and then oil was pumped in opposite direction at a constant flow rate (0.5 ml/min) with a periodic temperature reduction (by one degree every three hours) in core holder. The results of filtration study are shown in Figure 9.

Figure 9. Dynamics of pressure gradient change of oil filtration through core sample after pumping oil with AS inhibitor (0.5% wt) in case of periodic temperature reduction (from 39°C to 29°C)

Results of the study showed that AS inhibitor during injection into the bottomhole formation zone adsorbing on pore walls of reservoir rocks, is able to reduce paraffin saturation point in reservoir (by 6°C for test oil), thus avoiding early formation of solid paraffin particles in pore space of productive formation. Also, gradually being washed away from BFZ by produced fluid, AS inhibitor passes to well underground equipment, preventing formation of these sediments in well.

**CONCLUSIONS**

1. With the help of filtration experiment we managed to determine that paraffin saturation point in pore space of reservoir may exceed paraffin saturation point in free volume by a few degrees (by 6-9°C for test oil) that must be taken into account predicting risk of complications associated with AS formation, as well as when selecting methods and technologies for their prevention.

2. It was found that injection of AS inhibitor with depressor effect into wellbore fluids will be effective in case of dosing before beginning of solid paraffins formation, so supply of inhibitor into bottom hole in case when phase transition of paraffin began in reservoir will not be effective.

3. Study of adsorption and desorption processes of AS inhibitor in rock sample allowed to determine optimal
time of reservoir treatment by inhibitor, effective concentration of inhibitor during injection into BFZ, as well as duration of inhibitor desorption from reservoir.

4. Injection of AS inhibitor solution into BFZ will reduce paraffin saturation point in pore space of reservoir. Use of BFZ as natural batcher of AS inhibitor will allow not only to prevent sedimentation of paraffin in reservoir, but also to carry out supply of inhibitor into oil before beginning of paraffin crystallization in it.

REFERENCES


