Change of physical and chemical properties of asphaltene-resin-paraffin deposits deposits in tubing

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Abstract. The paper analyzes the geological and physical characteristics of the White Tiger field, deep and estuary samples of oil and asphaltene-resin-paraffin (ARP) deposits, which revealed the main factors leading to the intensive accumulation of asphaltenes on tubing surface during oil production. First of all, these are high formation temperatures (80-120°C) in combination with high paraffin separation temperature (57°C) and a relatively large oil depth (up to 4,500 m). Experimental studies were carried out and chemical reagents consisting of a mixture of polyvinyl acetate and organic solvents were selected (naphthalene, toluene, aromatic derivatives), which affect paraffin separation, which, in turn, leads to a decrease in viscosity and dynamic shear stress at the same temperature, as well as a decrease in oil congelation temperature thereby promoting the inhibition of asphaltene-resin-paraffin deposits by interacting with an activator for gel formation, adsorption on the surface of rocks, i.e. preventing the formation of asphaltene during oil production.

Keywords: asphaltene-resin-paraffin deposits, dewaxing, chemical composition, acid, solvent, experiment, chemical reagent, activator, modeling.

1. Introduction
The management of oil fields development implies optimal decisions to improve technical and economic indicators [1-4]. The reduction of risks of inefficient decisions is based on the use of a scientific and methodological base, which is formed by studying the processes occurring in a formation, bottomhole zone, tubing, etc. [5-10].

An important point here is the problem of asphaltene-resin-paraffin deposits in tubing and their control [11].

The White Tiger field is characterized by high-wax oil with a high content of resins and asphaltenes. All this creates a number of serious problems. One of the main factors complicating the operation of wells is the deposition of asphalt-resin-paraffin substances on the surface of downhole equipment, which decreases the time between overhauls, as well as the efficiency of the operation of the production well stock.

ARP deposits are formed mainly by paraffins, resins and asphaltenes, which are dissolved by colloids in oil in situ.
According to the reports on well shutdowns, 418 well operations were performed to clean downhole and wellhead equipment from ARP deposits associated with well shutdown. Data on the amount of dewaxing for wells and at offshore fixed platforms (OFP) are presented in Table 1.

The parameters of the wells typical in terms of ARP and the plan-schedule for dewaxing of wells of the White Tiger field show that the largest number of well operations for ARP liquidation was carried out at OFP-5 (223 well operations) and at OFP-10 (110 well operations).

Table 1. Cleaning of downhole and wellhead equipment from ARP

| OFP / Block conductor | Well number | Operation facility | Production method | Parameters | Water cutting, % | Q, t/d | Q, t/d | Well number | Downtime, h | Oil production, t | Losses | Number of operations, wells | Number of operations at OFP |
|-----------------------|-------------|--------------------|-------------------|------------|-----------------|--------|--------|-------------|-------------|-------------------|---------|--------------------------|--------------------------|
| 3                     | 61          | LO g/l             | 19                | 59         | 6               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 3                     | 71          | LM g/l             | 40                | 67         | 11               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 3                     | 107         | LM g/l             | 100               | 55         | 36               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 3                     | 193         | LO g/l             | 31                | 0.9        | 29               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 3                     | 68          | LO g/l             | 77                | 27         | 45               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 5                     | 104         | LO g/l             | 14.4              | 25         | 8.6              | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 5                     | 108         | LO g/l             | 20                | 2.1        | 15               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 5                     | 503         | LO g/l             | 34                | 5.8        | 26               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 5                     | 507         | LO g/l             | 45                | 58         | 15               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 5                     | 509         | LO g/l             | 44                | 60         | 14               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 5                     | 510         | LO g/l             | 64                | 36         | 33               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 7                     | 704         | UO g/l             | 704               | 1          | 9                | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 7                     | 710         | LM g/l             | 29                | 11         | 20               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 7                     | 715         | LO g/l             | 22                | 37         | 11               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 10                    | 1002        | LO g/l             | 24                | 1.8        | 19               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 10                    | 1013        | UO g/l             | 18.5              | 1.3        | 14.4             | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 10                    | 1014        | UO g/l             | 72                | 3.5        | 55               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 10                    | 1016        | UO g/l             | 28                | 0.5        | 22               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 10                    | 1021        | F g/l              | 36                | 0          | 28               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 10                    | 1022        | LO g/l             | 79                | 4          | 60               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 10                    | 1023        | LO g/l             | 49                | 2.8        | 38               | 5      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |
| 11                    | 1120        | LO g/l             | 25                | 7.6        | 19               | 1      | 59     | 70          | 1           | 1                 | 17      | 1                        | 23                      |

**Note:** g/l – gas lift; LO – Lower Oligocene; LM – Lower Miocene; UO – upper Oligocene; F – foundation.

The problem wells, where most of the dewaxing operations are performed, are the wells of the White Tiger field with oil flowrate from 9 to 60 tons/day and watercut from 0 to 60%, operated by a compressor gas lift. Regular dewaxing (from one to several times a month) mainly involves wells operating from the lower and upper oligocene.

Dewaxing was carried out on 22 wells, well downtime due to dewaxing amounted to 1,197 hours and at the same time oil production losses amounted to 1,087.7 tons of oil. The largest well downtime...
and oil production losses are observed at OFP -5 (565 hours and 426 tons) and OFP -10 (3,116 hours and 424 tons).

The defined chemical composition of ARP samples taken from the well tubing is shown in Table 2.

| Sample number | Composition of deposits | Content, % wt. |
|---------------|-------------------------|----------------|
| 1             | paraffine               | 33.2           |
| 2             | resin                   | 3.7            |
| 3             | asphaltene              | 1.2            |
| 4             | mechanical impurity     | 0.1            |
| 5             | light oil               | others         |

The analysis of geological and physical characteristics of the White Tiger field, downhole and wellhead samples of oil and ARP revealed the main factors contributing to the intensive accumulation of solid phase (in particular, ARP) on the surface of tubing during oil production. First of all, these are high formation temperatures (80-120°C) in combination with high paraffin separation temperature (57°C) and a relatively large oil depth (up to 4,500 m). These factors contribute to the formation of ARP on tubing surface from a depth of 1,000 m. This is complicated by the fact that the waxing process of the equipment is intensified by a high content of paraffins and resins in oil in combination with the roughness of the tubing surface. As a result, strong ARP are formed, which are well bonded to each other and to the tubing surface.

Besides, during operation of wells when pressure is reduced to saturation pressure and lower, when the production rises, oil is degassed and cooled, which increases the intensity of wax deposition.

During operation of wells the internal flow section of pipes is reduced up to emergency situation – rod wax.

The studies of the state of ARP deposits in gas lift wells of the White Tiger field make it possible to draw the following conclusions.

The accumulation of ARP in the internal surfaces of tubing leads to the acceleration of equipment wear, decrease in the productivity coefficient of the field, so there is a need for preventive work to remove ARP paraffin deposits, their decomposition and formation.

2. Materials and methods

Until recently, the main methods for controlling ARP deposits were heat treatment, mechanical treatment (using scrapers of various configurations) and a chemical method. The heat treatment method is based on the ability of paraffin to melt at temperatures above 50°C, so special equipment is needed to create the necessary temperature.

The main disadvantages of the first 2 methods can be their high energy intensity due to the use of thermal steam units, unreliability, low efficiency and additional financial and labor costs.

The analysis of existing methods for controlling the formation of stable water-paraffin emulsions with ARP deposits shows that the chemical methods are the most promising. They provide for the use of reagents to remove already formed ARP deposits, prevent their deposition and destroy oil and water deposits. But the chemical method often leads to the problem of choosing a working solution taking into account the physicochemical parameters of oil in each field. This is caused by insufficient data on the mechanism of interaction of petroleum dispersion systems with surfactants.

In order to develop a technology for removing and preventing ARP deposits in tubing of the White Tiger wells, the studies were carried out to determine the physicochemical characteristics of ARP deposits extracted from the tubing of wells: melting temperature, surface study using an electron microscope scanner, paraffin distribution in the treated ARP deposit.

3. Results and Discussion

The analysis includes sample cooling in an air bath with temperature control. When the wax
solidifies, a plateau is formed on the cooling curve thus indicating the wax melting point (cooling curve) of the test sample.

During the experiment, the following chemical reagents were used:
- linear alkylbenzene sulfonic acid (ABS);
- acetic acid;
- solvent: xylene, kerosene and additions;
- amines: ethanolamine, ethylene diamine, N-butylamine, Di-N-butylamine.

The procedure of the experiment is based on the alternating reaction of the acid solution with amines. The experiment is conducted in the following order.
1. A glass vessel for thermal reaction is prepares.
2. Acid and alkali components (amines) are weighed separately according to the calculated amount in two different vessels:
   - the first vessel contains a mixture of two acids of acetic acid and linear alkylbenzene sulfonic acid. Both acids are mixed uniformly with each other;
   - the second vessel contains alkaline solution consisting of one of the amines.
3. The exact amount of solvent used for the reaction is weighed and the solvent is divided into two parts. The first part is poured into a vessel with a mixture of acids, mixed uniformly (mixture A is obtained); the rest is poured into the second vessel with the alkaline solution inside and mixed uniformly (mixture B is obtained). The amount of solvent, in addition to the problem of being a spray medium for reaction products, the dissolved amount of ARP, reduces the viscosity of the reaction mixture, which still plays an important role in reducing the level of evaporation of the amine mixture.
4. Mixture A is poured into the prepared vessel, a thermometer is installed into the vessel so that the holder of thermometer mercury is located in the reaction center, initial temperature is recorded. Mixture B is added gradually to the vessel with mixture A while mixing. The reaction takes place very quickly, the change in reaction temperature is observed until the temperature no longer increases, this corresponds to the maximum temperature.
5. The pH of the mixture is determined after the reaction with an indicator (for each amine or amine mixture used).

After the reaction with all amines is completed, the results are compared and the most rational amine that meets the specific criteria is selected.

The ability to dissolve ARP deposits with selected amine with different alkali-acid ratios and with different solvent compositions is determined by the weight loss method.

The experiment is carried out in sequence according to the above scheme, but after filling the vessel with mixture A, we use a specific mass of deposits thus fixing and immersing them in the vessel. After adding mixture B to the vessel, the reaction takes place for 5 minutes, after which the deposit sample is removed and the residual amount is weighed.

For the injection process, the mobility of the injected fluid is very important and directly affects the efficiency and performance of the process.

Since the wells in need of ARP removal treatment are mostly low-debit wells with some degree of watercut, viscosity is studied after adding certain amounts of water to the product to study the effect of the presence of water on the mobility of products after the thermal reaction.

For each sample of products after the reaction, when the deposits are already dissolved, the viscosity is determined by the gradual addition of certain amounts of water so as to obtain water concentrations respectively: 10; 20; 30; 40; 50; 60; 70; 80% and 90% (when water is added to the product after the heat reaction, it is necessary to mix the mixture evenly).

The following chemicals are used to remove and prevent the formation of ARP deposits:

1. **VD-Dewax A chemical reagent**.

   The VD-Dewax A reagent is a mixture consisting mainly of organic acid and organic solvents. Linear alkylbenzene sulfonic acid (ABS) and acetic acid are basic acids that react with alkali as part of the VD-Dewax A reagent with the release of heat that melts ARP in tubing.

   The mixture of organic solvents as part of VD-Dewax A is intended to dissolve ARP melted by heat.
generation, which helps them to disperse well in the liquid phase after lowering the temperature of the reaction (thermosetting ends).

The technical parameters of VD-Dewax A chemical reagent are shown in Table 3.

2. **VD-Dewax B chemical reagent.**

The VD-Dewax B chemical reagent is a mixture consisting mainly of an organic amine and a mixture of organic solvents.

The organic amine solution is alkaline and can react with the organic acid of VD-Dewax A to form a large amount of heat to melt ARP in tubing.

**Table 3. Technical parameters of VD-Dewax A**

| Technical parameters    | Value            |
|-------------------------|------------------|
| Color                   | Light brown      |
| ABS concentration, %    | ≥ 25             |
| Acetic acid concentration, % | ≥ 25         |
| Relative weight (at 20°C), kg/m³ | 921–929       |
| pH                      | 1                |

The organic solvents as part of VD-Dewax B are designed to dissolve molten ARP, which allows them dispersing well in the liquid phase after thermochemical reaction and lowering the temperature of the medium. The technical parameters of VD-Dewax B are shown in Table 4.

**Table 4. Technical parameters of VD-Dewax B**

| Technical parameters        | Value          |
|-----------------------------|----------------|
| Color                       | No color / Light yellow |
| Concentration of organic amines, % | ≥ 50        |
| Relative weight (20°C), kg/m³ | 740–750      |
| pH                          | 10–11          |

3. **PPD (VX7484) chemical reagent.**

The PPD VX7484 chemical reagent is a mixture of polyvinyl acetate and organic solvents: naphthalene, toluene, aromatic derivatives (Table 5).

The PPD chemical reagent consists of a mixture of polymers in aromatic solvents, impacts paraffin separation, which leads to a decrease in viscosity and dynamic shear stress at the same temperature, as well as a decrease in oil congelation temperature.

The PPD VX7484 is designed to inhibit the formation of ARP by interacting with an activator to form a gel, adsorption on the surface of rocks, i.e. preventing the formation of ARP during oil production.

**Table 5. Technical parameters of PPD VX7484**

| Technical parameters                      | Value                  |
|------------------------------------------|------------------------|
| Color                                    | Amber                  |
| Odor                                     | Aromatic hydrocarbon   |
| Density (15.6°C)                         | 0.881                  |
| Water solubility, %                      | Indissolubility        |
| Percentage of light evaporation of hydrocarbons, % | 71.2                |
4. **VDA 11 activator.**

The VDA 11 activator is a mixture of alcohols, physically interacts with PPD converting PPD from a liquid phase into a gel phase with its absorption by the rock surface. Technical parameters of VDA 11 activator are given in Table 6.

| Technical parameters | Value       |
|----------------------|-------------|
| Color                | No color, transparent |
| Alcohole concentration, % | 100         |
| Relative weight (20°C), kg/m³ | 790–791.8 |

The development of the ARP treatment technology for removal is followed by the development of technology for the prevention of ARP re-deposition. For this purpose, a chemical system is selected, which consists of the PPD chemical reagent and an activator. First, it is necessary to determine the temperature of crude oil solidification with and without PPD and at different concentrations. Crude oil temperature measurements are performed according to the ASTM-D97 standard. A graph of the crude oil solidification temperature versus the concentration of the added PPD is determined. This plays an important role in further evaluation of the effectiveness of the model in squeezing PPD and activator.

An experimental scheme for modeling the process of ARP deposits inhibition in production wells is shown in the figure 1.

![Figure 1. Experimental scheme for modeling the process of ARP deposit inhibition in production wells: 1 – column of porous material; 2 – barrel of crude oil; 3 – heater; 4 – heater shoe; 5 – heater of a porous material column; 7 – pipe for feeding crude oil into a column of porous material; 8 – valve/switch of crude oil flow control; 9 – vessel for commercial oil show from the column of porous material](image)

Experimental modeling of ARP deposit inhibition in production wells is carried out according to the following scheme:

1. **Preparation of the squeezing model:**
   - a high porosity material, such as sand, is filled into the vessel (1), set according to the scheme, and the porous material is saturated with surfactant oil;
   - a calculated amount of dissolved activator and solvent is pumped into the column of porous material through a tube (7);
- a buffer solution is pumped again to isolate the PPD chemical and the activator in the column;
- a mixture of PPD and oil is pumped (the ratio of crude oil has already been calculated);
- PPD is mixed with the activator within the porous material and deposited on the surface of the porous material in a column (1).

2. Procedure for crude oil injection with PPD:

The crude oil not containing PPD chemical reagent (its solidification temperature is determined earlier) is pumped in a vessel (2) and after heating to 65°C it is pumped into a column (1) through a tube (7). Oil flow is controlled by a valve (8) in order to increase the time of contact in the column with porous material containing PPD. The column temperature is maintained by the heater (6). Crude oil flows upwardly into the vessel (9) after passing the porous material containing PPD. The solidification temperature is periodically checked in the obtained sample in the vessel (9). The process is repeated until the value of the solidification temperature of commercial oil becomes equal to the solidification temperature of the initial crude oil. The total volume of produced commercial oil (total amount of oil passing through the column) is determined.

The corrosion aggressiveness of the chemical system is determined using the Cortest autoclave (USA) according to the ASTM G-103 standard.

The following materials and equipment were used to determine the corrosion aggressiveness by the weight loss method: autoclave; nitrogen cylinder; three metal samples (P110); chemical reagents (interact with each other to release heat) – VD-Dewax A and VD-Dewax B in the volume of 2·10⁻³ m³.

The corrosion aggressiveness by the weight loss method is determined as follows.
1. Clean and dry the autoclave chamber (for the sample).
2. Clean the surface of metal samples R110 to completely remove the oxide layer on the surface and determine the initial mass (m₀).
3. Pour the chemicals into the autoclave chamber.
4. Hang the metal sample in place, close the blind flange of the autocalve chamber.
5. Switch on the controlled button and set the test mode: temperature – 120°C, pressure – 5.0 MPa.
6. After a certain time (predetermined), remove the sample, wash, dry to a constant mass and determine the mass (m₁).
7. Determine the weight loss of samples: W = m₀ – m₁.
8. Calculate corrosion rates for 3 samples and determine the average value.

The corrosion rate is determined by the following formula:

\[ L = \frac{K \cdot W}{A \cdot T \cdot D} \]

where \( W \) – weight loss of the metal sample after treatment, kg; \( A \) – initial area of the metal sample, m²; \( T \) – sample dipping time, hour; \( D \) – metal density, kg/m³; \( K \) – coefficient that depends on the unit of speed (if the unit of corrosion rate is 10⁻³ m/year, then \( K = 8.76 \times 10^9 \)).

4. Conclusion

1. The analysis of geological and physical characteristics of the White Tiger field, downhole and wellhead samples of oil and ARP revealed the main factors contributing to the intensive accumulation of ARP on tubing surface during oil production. First of all, these are high formation temperatures (80-120°C) in combination with high paraffin separation temperature (57°C) and a relatively large oil depth (up to 4,500 m).

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