The influence of the ARPD composition on the heat of dissolution in hydrocarbon solvents

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Abstract. In this paper, we studied two samples of asphaltene-resin-paraffin deposits of different composition, precipitated during the extraction of hard-to-recover oil and characterized by different melting points. The samples were studied by the thermal analysis method on the MOM (Hungary) Q-1500D derivatograph. The compositions of samples were studied by SARA-analysis by taking into account the methodical recommendations of ASTM D4124-09 and GOST 32269-201. The process of asphaltene-resin-paraffin deposits dissolving in straight-run fractions was studied. Straight-run fractions 80-180°C and 180-350°C were used for heat dissolution experiments. The heat of dissolution of asphaltene-resin-paraffin deposits in fractions was measured on a calorimeter. The graphs that indicate the dependence of the heat of dissolution of asphaltene-resin-paraffin deposits on its concentration in fractions were plotted. The efficiency of the dissolution process was determined.

1. Introduction

The formation of asphaltene-resin-paraffin deposits on the walls of pipelines, oilfield equipment and lifting pipes causes some negative consequences such as equipment wear, reducing the effective diameter of pipelines, plugging of wells and increasing the cost of electricity and equipment repairs. Prevention of the formation of asphaltene-resin-paraffin deposits (ARPD) by physical and chemical methods at the moment does not allow to completely stop the precipitation of paraffin, therefore their removal are being performed in various methods. One of these methods is by heating or thermal reaction, based on the ability of paraffin to melt at temperatures above 50°C and be carried out from a heated surface in a fluid flow [1]. To create the required melting point, special heat sources are needed, which can be hot oil or water as the heat transmitter, superheated steam, various electric furnaces and induction preheaters. Some reagents can also be included here during the interaction with which exothermic reactions take place [2]. When choosing heat sources, they are considered based on the composition of the extracted oil, the heating zone, economic conditions and its feasibility (power consumption) [3].

Due to high energy usage and uncontrollable heat release, a method using reagents based on exothermic reactions is usually used only at fields for cleaning open reservoirs of small volumes containing watered sludge [1].
Two other thermal methods which are: the use of hot oil by pumping it around the piping of the well (the surroundings of the pipe) or by directly pumping it into the pipe and the use of electrical furnaces for heating, have been widely used in industries. The advantages of using hot oil include: heating the well to a higher temperature in comparison with other applied agents (steam, water) which as they deepen, lose their temperature by heating the surrounding rock. Furthermore, the use of hot oil helps to heat wells with paraffin plug without mechanical damage to the column. The disadvantages of using hot oil as a thermal method for removing asphalt–resin-paraffin deposits are: high energy consumption and the well becomes an idle well during treatment. When removing and preventing the ARPD at the Mamontov’s oil field, which is operated by the Russian oil company RN-Yuganskneftegaz, along with the chemical method, the thermal method of removing asphalt-resin-paraffin substances are the most widely used, precisely the use of hot oil and heating electrical cables [4]. Tatneft at the Matrosov’s oil field, in addition to the use of inhibitors and the use of polymer epoxy coatings, also adheres to the technology of pumping hot oil and water in the piping of the well [5]. This method of removing ARPD is also used by companies SURGUTNEFTEGAZ and LUKOIL-PERM on its oilfields. Washing the well equipment and tubing with hot oil using a special unit for deparaffinization the ADPM wells, creating a local heat flow in the piping using deep electric heaters [6-9].

There is another type of the thermal method, which is the induction heating. This method is based on the formation of a thermal field on a conducting body [10-12]. For example, in the piping wall, this technology uses the heating of bodies in the electromagnetic field due to the thermal effect of the electric current flowing directly through the heated body and excited in it by electromagnetic induction. The released heat in this thermal method is transferred to the fluid flowing around the heating element and prevents it from cooling. The induction heating method was successfully tested in the fields of Western Siberia, the Republics of Bashkortostan and Tatarstan by company GAZPROMNEFT-KHANTOS [13]. As a result of such an impact, the average well flow rates increased by 12 % and the use of other methods of ARPD removal, both chemical and physical methods were greatly decreased and that tremendously helped to reduce expenses.

Regardless of some existing disadvantages of thermal methods of ARPD removal which includes: heat loss while flushing wells with hot oil, high energy costs when using electric furnaces and fire hazard during exothermic reactions. Thermal methods of controlling ARPD are used not only to remove, but also to prevent the formation of ARPD. Thus, this method is effective in two ways, which is its main advantage.

From the above given considerations, the two methods of combination of chemical and thermal has a great prospect and it is very relevant to study.

From a practical point of view, it is of interest to study the efficiency of the action of solvents on the removal of paraffin deposits of different composition with increasing temperatures and identifying the optimum temperature.

2. Materials and Methods

Two ARPD samples with different characteristics were selected for study. The first ARPD is characterized by a softer consistency, it is greasy, with a content of mechanical impurities of 0.9 %. The second ARPD is more solid, it is characterized by a rigid structure with a mechanical impurity content of 4.9 %.

The samples were studied by the thermal analysis method on the MOM (Hungary) Q-1500D derivatograph in the temperature range 20-1000 °C with a furnace heating rate of 10 °C/min. The
atmosphere in the furnace is stationary. Aluminium oxide was used as an inert substance. In the experiments, a platinum crucible was used. The sample weight was 100 mg. Each experiment was carried out 2-3 times. The measurement error of the temperature was ± 0.2 °C, thermal effects – 4 %.

SARA analysis was made for these two samples. Separation by the SARA method is carried out by taking into account the methodical recommendations of ASTM D4124-09 and GOST 32269-2013 in several stages. This method is based on the separation of crude oil into four groups of compounds: saturated hydrocarbons, aromatic compounds, resins and asphaltenes (SARA) according to their solubility and polarity.

Initially, asphaltenes was precipitated by hexane with appropriate preparation of maltens. From maltens three groups (saturated hydrocarbons, aromatics and resins) were got that were separated by using a glass chromatography column by successively eluting with aliphatic and aromatic hydrocarbons from the adsorbent dehydrated neutral aluminum.

The heat of dissolution was measured on a calorimeter with direct registration of the temperature increase and with the subsequent determination of the thermal value of the calorimetric system. The design of the calorimeter with an isothermal shell allows controlling the heat transfer.

3. Results and Discussions

3.1. SARA group composition

The results of the determination of the composition group of the test samples by the SARA method are given in Table 1.

| Objects   | Group composition (SARA), wt % |
|-----------|--------------------------------|
|           | Saturates | Aromatics | Resins | Asphaltenes |
| Deposit 1 | 57.8       | 31.6       | 7.0    | 3.6          |
| Deposit 2 | 51.2       | 33.8       | 9.2    | 5.8          |

According to data from the table 1 sample 1 differs from the sample 2 by the higher content of saturates and less content of aromatics, resins and asphaltenes. Both samples have got high content of resins and asphaltenes.

High molecular paraffinic hydrocarbons of ARPD are involved in the formation of sediments not only due to dispersion forces, but also due to the contribution of polar structures of hybrid components. They are part of Saturates (Table 1). The presence of resins and asphaltenes leads to a significant increase in the viscosity and hardness of ARPD due to the formation of associates, which significantly complicates the process of their removal.

3.2 Thermal analysis

There are thermal analysis curves for the sample 1 on the figure 1.
Fig. 1. Thermal analysis curves for the first sample.

The endothermic peak on the DTA curve corresponds to the absorption of heat during the melting of solid paraffins. At the same time, on the TG curve this peak corresponds to a flat area, as the mass of the sample doesn’t, only heat absorption occurs. We take the extremum of the endothermic peak as the true melting point of solid paraffins, although the peak can be characterized as consisting of paraffins of different molecular weight. To determine the melting temperature of the extremum we drop a perpendicular on the curve of the temperature change T. When the perpendicular is deposited on the abscissa axis, we obtain a melting point equal to 62°C. The loss of mass by the stages of thermal-oxidative destruction allows to indirectly characterize the fractional composition of ARPD. The second sample of ARPD is characterized by a higher melting point of 78°C.

3.3 Data on the dissolution of ARPD

The temperature and concentration dependences of the heat of ARPD dissolution in various straight-run hydrocarbon fractions in the system were obtained.

The influence of the composition and concentration of ARPD on the heat of their dissolution in fractions of 80-180 °C and 180-350 °C was determined (figure 2).

As figure 2 shows, all the dependencies are extreme in nature with a different location of the maximum. Moreover, when they are dissolved in a fraction of 80-180 °C, ARPD-1 has a maximum thermal effect with a high content of solid paraffin hydrocarbons. In addition, the maximum value of the thermal effect for ARPD-1 is shifted towards higher concentrations, which indicates a greater capacity of the 80-180 °C fraction with respect to these types of ARPD.

When asphaltene-resin substances increase in the ARPDs, both the thermal effect and the capacity relative to the 80-180 °C fraction decrease. When molecular weight of fraction 180-350 °C increases,
the heat effect of dissolution of the ARPD-1 (paraffin base) decreases and the thermal effect of dissolution of the ARPD-2 increases (with the increase of content of the asphaltene-resin substances). At the same time, the maximum values of the thermal effect of dissolving ARPD-2 are shifted towards higher concentrations.

![Figure 2. Dependence of the heat of dissolving ARPD in hydrocarbon fractions from concentrations.](image)

4. Conclusion

We obtained and studied two samples of asphaltene-resin-paraffin deposits which were formed during oil production. The phase equilibrium in petroleum systems was shown by thermal analysis method. The method of thermal analysis allowed us to estimate the melting point of asphaltene-resin-paraffin deposits and characterize the composition of solid paraffinic hydrocarbons by the endothermic peak and the DTA curve on the thermogram. Informative indicators for choosing the asphaltene-resin-paraffin deposits removal method can be the melting point, the melting curve of paraffins in a hydrocarbon solution, and the heat of asphaltene-resin-paraffin deposits dissolution in a solvent. Melting point could characterize the qualitative composition of the individual components in the asphaltene-resin-paraffin deposits or the dissolving properties of the medium. Point of paraffin emergence and point of paraffin disappearance for paraffinic crude oil were shown at thermal curves.

The factors influencing on heat dissolution of the samples with application of straight-run fractions as solvents were presented. The results can be used to predict asphaltene-resin-paraffin deposition from crude oil during its production and refining and also to select proper methods to remove of asphaltene-resin-paraffin deposits.

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