Specific Features of the Composition of Petroleum from the Usinsk Oil Deposit

I Korol1, T Petrenko2, D Chuikin2

1Institute of Petroleum Geology and Geophysics A.A. Trofimuka SB RAS, Tomsk branch, Tomsk, pr. Akademichesky 4, 634055, Russia
2Institute of Petroleum Chemistry SB RAS, Academic 4, Tomsk, 634055 Russia

E-mail: KorolIS@ipgg.sbras.ru

Abstract. The research studied petroleum from Permian-Carboniferous fields from the Usinsk oil deposit in the north-east of the Komi Republic, Russia, well-bores No. 5339 (middle production zone) and No. 2956 (upper and middle production zone). Permian-Carboniferous petroleum has high viscosity (up to 11980 MPa*s), density (up to 0.987 g/cm3), average grade of sulphur (up to 2.5% mass) and are hard to recover. The element, component and micro-element composition of the petroleum and its fractions was established. The share of vanadyl and nickel porphyrins was measured by chromatographic separation. The research has established that the petroleum and fractions from the Usinsk oil deposit are a complex mixture of hydrocarbons and hetero-organic compounds with an elevated aromatic level and with oxygen-containing compounds playing the most important part. Total content of micro-elements in the studied samples does not exceed 0.5% mass of the petroleum's mass. The concentration of micro-elements in petroleum is reducing in this order: Cl, Ca, Na, V, Ni, Mg, Fe, Si, Ba, Cs, Cu, Zn, Mn, Co, Cd, P. The share of vanadyl porphyrins (VO-P) is higher than that of nickel porphyrins (NiP). The distribution of VO-P by fractions for the petroleum in both well-bores is the same and reduces in terms of resins-asphaltens-oils. The distribution of NiP does not have a clear correlation. This distribution can be associated with the chemical composition, thermodynamic and kinematic stability.

1. Introduction

According to various estimates, petroleum contains more than 60 different elements, and metal-organic compounds and trace and rare elements account for the majority of them. Non-organic micro-elements in petroleum along with genetic indicator values are important from environmental and industrial point of view. Today the number of publications that study the changing content and control of the elemental composition during hydrocarbon production is rather low.

This article explores the petroleum from well-bores No. 5339 (middle production zone) and No. 2956 (upper and middle production zone) from the Usinsk oil deposit. The Permian-Carboniferous oil deposit from the Usinsk oil deposit is situated in the north-east of the Komi Republic, Russia. In terms of production, the deposit is divided into three facility: upper, middle and lower. The Permian-Carboniferous petroleum has high viscosity (up to 11980 MPa*s), density (up to 0.987 g/cm3), average grade of sulphur (up to 2.5% mass) and are hard to recover [1, 2]. The publication presents the element, component and micro-element compositions, and the share and distribution of vanadyl and nickel porphyrins in oils and fractions from the Usinsk oil deposit are established.
2. Materials and methods

For the purposes of the research, the mechanical impurities and water from the petroleum samples were consistently removed by centrifugation and sedimentation over heat-treated calcium chloride. The component content (oils, resins, asphaltens) of the petroleum samples was studied through sedimentation and chromatography methods. Asphaltens were extracted by the Golde method. Deasphalting agent was applied over silica gel ("ACKT" trade mark) in the Soxhlet extractor, then by multiple hot extraction with hexane from adsorbent oils were desorbed, and then resins were desorbed by a mixture of alcohol and chloroform (7:93). The elementary composition was established with the help of a CHNS-analyser "Vario EL Cube". The share of oxygen was measured by the difference between 100% and the sum of the elements C, H, N, S. IR spectrum of petroleum fractions were registered by a FTIR spectrometer NICOLET 5700 in the range of 4000…400 cm⁻¹. The content of micro-elements was measured by X-ray fluorescence analysis method using an wave x-ray fluorescent spectrometer "ARL PERFORM'X 4200". The quantity analysis of metal porphyrins was established by the method of electronic spectroscopy using a UVIKON 943 spectrophotometer and second-order derivative spectrophotometry. The concentration of metal porphyrins complexes was calculated using the methodology [3], with absorption band intensity at 550 nm for nickel porphyrins (NiP) and at 570 nm for vanadyl porphyrins (VoP).

3. Results and discussion

We know that depending on the conditions (pH, temperature, pressure, etc.), petroleum can selectively extract and accumulate many micro-elements from contacting ores and layer waters. The prevalence of micro-elements seems to be an individual characteristic of the petroleum from every oil-bearing field that is formed under the influence of many factors during the whole geological history of a carbon hydrate field [4].

The elemental analysis (Table 1) of the petroleum and fractions from the Usinsk deposit are a complex mixture of hydrocarbons and hetero-organic compounds. The ration H/C changes from 1.16 to 1.57, which is characteristic for compounds with an elevated aromatic level, and in terms of the content of S, N and O the studied petroleum is enriched by heteroatomic components. High concentration of oxygen and lower concentration of sulphur and nitrogen in the sample indicates that oxygen compounds account for the majority.

| sample          | Elementary composition, % mass | H/C   |
|-----------------|--------------------------------|-------|
| well-bore No.   | C     | H     | S     | N    | O     |       |
| 2956            | 83.78 | 9.92  | 2.06  | 0.97 | 3.27  | 1.42  |
| oils            | 84.48 | 10.97 | 1.49  | 0.56 | 2.5   | 1.56  |
| resins          | 81.73 | 9.81  | 2.14  | 1.24 | 5.08  | 1.44  |
| asphaltens      | 83.51 | 8.05  | 2.68  | 1.58 | 4.18  | 1.16  |
| well-bore No.   | C     | H     | S     | N    | O     |       |
| 5339            | 83.19 | 9.75  | 1.90  | 1.00 | 4.16  | 1.41  |
| oils            | 83.78 | 10.97 | 1.58  | 0.54 | 3.13  | 1.57  |
| resins          | 80.65 | 9.55  | 2.21  | 1.22 | 6.37  | 1.42  |
| asphaltens      | 83.16 | 8.03  | 2.06  | 1.58 | 5.17  | 1.16  |

The authors [5, 6] have established that the stability of petroleum is affected by the component, structural and group and micro-element compositions. [7] demonstrates that the petroleum from the Usinsk oil deposit shows a trend toward the changing component content when secondary extraction methods are employed (gel petroleum displacement composition processing). The research of the
component composition (oils, resins, asphaltens) indicated that the sample from the upper facility (UF) has more oils and less resins and asphaltens than the middle facility (MF). The study of the structural and group composition of the explored samples using the IR spectroscopy showed that oils are almost completely similar in terms of paraffin structures, long alkane chains and condensed arenes.

Table 2. Composition of Usinks petroleums.

| Well bore №, facility | Contents, % mass |
|-----------------------|------------------|
|                       | oils             | resins | asphaltens |
| 2956, BO              | 76.3             | 17.0   | 6.7        |
| 5339, CO              | 72.0             | 20.2   | 7.8        |

Numerous studies show that the main salts in layer waters are chlorides of alkali and alkali earth metals [8]. Qualitative and quantitative contents of elements in the water from the studied well-bores 2956 and 5339 are enriched with chloride salts up to 57 mg/l and are represented by salts of Na, Ca, Mg, K, Sr. The content of water in the petroleum from well-bore No. 2956 is 28.19%, and in well-bore 5339 it is 29.56% mass, established according to National State Standard 2477-2014. After the water is removed from the oil samples, the content of metals (Ca, Mg, Na, Ba) reduces, and the concentration of other components changes within the range of analysis methodology error. The content of non-metals Cl, S, Si in the petroleum after water is removed, changes significantly (Table 2). It seems most likely that these elements in the initial sample were in an ionic form, and the change in the contents is determined by the removal of the water phase.

Table 3. Content of elements in the initial, dehydrated petroleum, oils, resins and asphaltens in the petroleum from the Usinsk oil deposit.

| Content, ppm |
|--------------|
| Well-bore    | 2956 petrol |            | 5339 petrol |
|              | initial     | dehydrated | initial     | dehydrated |
| S            | 20848       | 10325      | 1496       | 2146       | 6582.7     | 15997       | 7851       | 1590       | 2443       | 2678.9     |
| Cl           | 813.2       | 613.2      | 11.1       | 107        | 493.8      | 7128        | 6858       | 17.8       | 151.4      | 6588.9     |
| Ca           | 133.9       | 79.9       | 14.2       | 19.3       | 44.67      | 1392        | 987.5      | 29.3       | 345.5      | 593.3      |
| Na           | 90.1        | 87.7       | 10.4       | 28.9       | 47.2       | 885.5       | 652.8      | 102.5      | 217.5      | 316.1      |
| V            | 72.6        | 71.9       | 1.1        | 11.5       | 57.3       | 51.4        | 51.2       | 1.4        | 22.3       | 27.5       |
| Ni           | 40.4        | 39.6       | 3.6        | 2.3        | 34.9       | 28.2        | 27.9       | 2.3        | 5.7        | 16.3       |
| Mg           | 40          | 35         | 8.45       | 10.2       | 23.3       | 748.4       | 428.9      | 10.1       | 34.51      | 378        |
| Fe           | 8           | 5          | 1.0        | 0.8        | 3.04       | 1.5         | 0.6        | 0.1        | 0.24       | 0.41       |
| Si           | 4.8         | 3.6        | 0.6        | 2.7        | -          | 3.6         | 2.46       | 1.7        | 0.59       | -          |
| Ba           | 2.9         | 1.9        | 0.7        | 0.28       | 0.58       | 7           | 5          | 1.5        | 1.2        | 2.42       |
| Cs           | 1.5         | 1.45       | 0.7        | 0.1        | 0.43       | 1.29        | 1.27       | 0.3        | 0.5        | 0.28       |
| Cu           | 0.4         | 0.4        | 0.3        | 0.1        | 0          | 0.6         | 0.68       | 0.21       | 0.305      | 0.163      |
| Zn           | 0.3         | 0.27       | 0.1        | 0.1        | -          | 0.5         | 0.44       | 0.4        | 0.02       | -          |
| Mn           | 0.32        | 0.3        | 0.1        | 0.204      | -          | 0.17        | 0.1        | 0.1        | -          | -          |
| Co           | 0.3         | 0.3        | 0.1        | -          | -          | 0.1         | 0.1        | 0.1        | -          | -          |
| Cd           | 0.1         | 0.1        | 0.026      | 0.061      | -          | 0.1         | 0.1        | 0.032      | 0.05       | -          |
| P            | 0.1         | 0.1        | 0.55       | 0.14       | -          | 0.1         | 0.1        | 1.7        | 2.6        | -          |

M - oils, C - resins, A - asphaltens.
Heavy metals in hydrocarbon raw materials are widely represented. Today about 15-20% of the extracted hydrocarbons have toxic elements as impurities in their content that exceed the safe concentration, and the volume of such hydrocarbons is growing every year [9]. Heavy metals get through to the surface, when hydrocarbons are extracted with the most important ones being: V, Ni, Fe, Al, Cu, Mg, Ti, Co, Cr, Ba, Mn, Pb, Hg, Mo, etc.

According to the up-to-date data [10], mean concentration of micro-elements in petroleum reduces in the following order: Cl, V, Fe, Ni, Na, K, Mg, Si, Al, I, Br, Hg, Zn, P, Mo, Cr, Sr, Cu, Co, Mn, Ba, Se, As, Ga, Cs, Ge, Ag, Sb, U, Re, La, Sc, Pb, Ti, Sn, etc. The petroleum we studied in well-bore No. 2659 and No. 5339 are consistent with the trend with the concentration of micro-elements reducing in the following order: Cl, Ca, V, Ni, Mg, Fe, Si, Ba, Cs, Cu, Zn, Mn, Co, Na, Cd, P. Total content of micro-elements in the studied samples does not exceed 0.5% mass of the petroleum's mass. The micro-element composition of the initial and dehydrated petroleum and fractions in the studied well-bores is shown in Table 3. The content of elements after the division reduces in terms of oils-resins-asphaltens for both samples. The maximum content of Fe, Ni, V was found in asphaltens, while for Si and P it was oils and resins. As metals can form organic and non-organic compounds, that petroleum consists of [9], their distribution will be affected by the structure of petroleum compounds that can interact with them and form strong connections. This is why the assumption that many heavy metals got into petroleum from contacting ores and waters should be taken into account, and additional research is needed to provide more details.

Among metals V and Ni should be under special focus. In fossil fuels they are also represented as VOP and NiP metal complexes. The interest in metal porphyrins is mostly determined by fundamental issues of organic geochemistry, they are considered to be biomarkers, their structure is quite well-researched and described in various publications [11]. Despite petroleum metal porphyrins being well-researched, the questions of their practical use are still unanswered. For example, the article [12] shows that porphyrins complexes are catalytic reactive in the processes of petroleum refining. The authors [13] provide evidence that both types of metal porphyrins in the composition of asphaltens make a significant contribution in the surface activity of petroleum. VOP and NiP are found in dehydrated petroleum, asphaltens, resins and oils (Table 4). The distribution of VO-P by fractions for the petroleum in both well-bores is the same and reduces in terms of resins-asphaltens-oils. The distribution of NiP does not show any pattern, for example, for well-bore 2956 the maximum content of NiP was found in asphaltens with 9.91 n*mol/g, and in resins with 3.03 n*mol/g for well-bore 5339. This distribution can be associated with the chemical composition, thermodynamic and kinematic stability.

Table 4. Content of VO-P and NiP in the petroleum and fractions from the Usinsk oil deposit.

| sample      | Contents, n*mmol/g |
|-------------|---------------------|
|             | well-bore 2956  | well-bore 5339 |
|              | VO-P   | NiP  | VO-P   | NiP  |
| petrol      | 156    | 20   | 193    | 5    |
| oils        | 3.8    | 7.63 | 2.5    | 1.1  |
| resins      | 110    | 2.72 | 142    | 3.03 |
| asphaltens  | 41.5   | 9.91 | 48.6   | 1.1  |

The research has established that the petroleum and fractions from the Usinsk oil deposit are a complex mixture of hydrocarbons and hetero-organic compounds with an elevated aromatic level and with oxygen-containing compounds playing the most important part. Total content of micro-elements in the studied samples does not exceed 0.5% mass of the petroleum's mass. The concentration of micro-elements in petroleum is reducing in this order: Cl, Ca, Na, V, Ni, Mg, Fe, Si, Ba, Cs, Cu, Zn, Mn, Co, Cd, P. The share of vanadyl porphyrins (VOP) is higher than that of nickel porphyrins (NiP). The distribution of VO-P by fractions for the petroleum in both well-bores is the same and reduces in terms of resins-asphaltens-oils, the distribution of NiP does not show a clear pattern.
It is important to understand that the number of oil deposits is growing that call for new approaches to the extraction of hydrocarbon raw materials, both in terms of technological processes and environmental and economic costs associated with the extraction [14]. Accurate data is needed on the initial parameters and process control over the extraction in the field, which should result in a more rational organization of chemical production using hydro-mineral resources of oil deposits.

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