The Effect of EOR Technologies on the Composition of Recovered Crude Oil

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The effect of EOR technologies on the composition and properties of recovered crude oil was studied using crude oil from Usinskoye oil field (Komi Republic), which has high viscosity and high content of resins and asphaltenes. It is found that the Netrol system injection brings about an increase in the content of saturated hydrocarbons, asphaltenes and resins and a decrease in the content of aromatic hydrocarbons. As a result of the NINKA system injection, the saturated hydrocarbon content of crude would also increase, while the asphaltene and resin content would decrease. The application of the NINKA system in combination with thermal-steam treatment is found to cause an increase in the contents of saturated and aromatic hydrocarbons and reduction in the density of the studied crude oil.

Keywords: heavy-viscosity oils; EOR technologies; oil-displacement systems; group composition; saturated and aromatic hydrocarbons; organic acids; petroporphyrins

The production of heavy-viscosity crude oils in most oil fields of Russia is carried on using water shutoff technology. The EOR technologies used for the development of high-viscosity crude oil formations are based on water injection into the oil reservoir or on thermal-steam treatment of a net of injection wells. In point of fact, well flooding is displacement of crude oil from crumbling or porous rock. Crude oil production results in reservoir underbalance; therefore, the volume of injected water would make up for that of produced crude [1].

The commercially used EOR technology based on oil reservoir flooding has a number of advantages. However, this technology would not provide for complete oil recovery, especially when high-viscosity crude occurs in inhomogeneous porous rock, which might be due to the low conformance of flooded area. Generally, upon termination of oil formation development, the total of 40-60% of oil remains unrecovered.

The development of low-permeability reservoirs and high-viscosity oil formations poses a grave problem. This avenue of enquiry involves development of new techniques and refining of commercially applied physico-chemical methods, which would provide for reduction in the amount of produced water as well as for enhanced oil recovery.
New EOR technologies developed at the Institute of Petroleum Chemistry (Tomsk, Russia) are intended for the recovery of high-viscosity crude oils, which make up a large proportion of the total oil production. The use of technologies developed in combination with thermal-steam treatment methods permits reduction in crude oil viscosity and increase in oil displacement factor. Some of these methods employ thermotropic inorganic and polymer gels intended for the regulation of filtration flows, for increasing formation steam sweeping factor and for decreasing water cut of wells. Other methods employ surfactant-based systems, which cause generation of carbon dioxide and ammonia, thereby creating an alkaline buffer system. The systems developed, i.e. ‘GALKA’, ‘METKA’, ‘ROMKA’ and ‘NINKA’, are widely used commercially not only in Russia but also in other countries, e.g. China [2].

When used in combination, the above EOR technologies may cause chemical transformation of crude oil due to the exposure to high temperatures, to the action of carbon dioxide, ammonia or microorganisms and to the contact with high salinity brines. Oil displacement with water and residual oil recovery from low permeability reservoirs might also bring about certain changes in the composition and properties of native oil.

The goal of the present work is to study the effect of physico-chemical EOR technologies on the dynamics of variation in the composition of high-viscosity crude oils produced from Usinskoye oil field of the Permian-Carboniferous formation (Komi Republic).

Experimental

The studied crudes were produced from Usinskoye oil field of the Permian-Carboniferous formation. Three crude oil samples were collected from No. 3063 well at different time intervals after the Netrol system injection and three samples – from No. 6111 well, which had been subjected to the Netrol system injection followed by the NINKA system injection. Two more crude samples were obtained from No. 1073 well, which had been subjected to thermal-steam treatment followed by the NINKA system injection. Two test samples of native oil were collected from Nos. 3000 and 2983 wells, which are located, respectively, in the vicinity of Nos. 3000 and 2983 wells and which had not been treated by any physico-chemical methods, i.e. the Netrol and NINKA system injection or thermal-steam treatment [3].

Using the method of electron spectroscopy, the contents of petroporphyrins (vanadyl porphyrin and nickel porphyrin complexes) was determined for the extracts obtained from the crude oil samples using first alcohol and then acetone. Then the separation of both extracts was carried on by the method of liquid-adsorption chromatography on a column packed with Al₂O₃ (4th degree of activity); the eluents used were hexane, carbon tetrachloride, benzene and benzene-chloroform mixture in the volume ratio of 1:1. The petroporphyrins were examined with the aid of a spectrophotometer ‘SPECORD UV VIS’, using the adsorption band intensity in the visible region of the spectrum (550 nm for nickel porphyrin and 570 nm for vanadyl porphyrin) [4, 5].

The compositions of oil samples were determined by the method of liquid-adsorption chromatography of the deasphalted oil. The asphaltenes were removed by precipitation, using dry hexane in forty-fold excess (by volume) relative to the crude oil sample. The analysis was carried out on a column packed with two sorbents: SiO₂ (upper part) and Al₂O₃ (2nd degree of activity; lower part). The elution of saturated hydrocarbons, aromatic hydrocarbons and resins was carried on using hexane, benzene and
benzene-alcohol mixture in the volume ratio of 1:1. Upon solvent removal, the fractions were quantified gravimetrically.

The content of light fractions (% by mass; \( T_{bp} \leq 200^\circ C \)) was calculated from the difference between the original mass of the crude sample and that of oils, resins and asphaltenes.

Using alcohol solution of potassium hydroxide, potentiometric titration was carried on to determine the carboxyl group content of organic acids of the crude oil samples [6]. The contents of COOH- groups \((a)\) and free organic acids \((b)\) (% by mass) were calculated as

\[
C_{\text{COOH}} = \frac{(V_t - V_o) \times N_t \times 45/10 \times m}{(a)}
\]

\[
C_{\text{acid}} = C_{\text{COOH}} \times \frac{\text{MM}}{45} \quad (b)
\]

where \( V_t \) – the volume of potassium hydroxide solution (ml) used by titration of the crude sample up to the equivalence point;

\( V_o \) – the volume of titration agent solution (potassium hydroxide; ml) used for titration of blank solvent;

\( N_t \) – the concentration of titration agent solution (potassium hydroxide; mole/l);

\( 45 \) – COOH-group equivalent;

\( m \) – the original mass of crude sample (g);

\( \text{MM} \) – the molecular mass of organic acids (300 a.m.u.).

Finally, the aromatic hydrocarbons were analyzed using gas chromatography-mass spectrometry (GC-MS). The analyses were made on the device R-10-10C of the ‘NERMAG’ Company (France). The device features direct coupling with the capillary column; the mass-analyzer employs no retainer. The chromatograph features a ‘SUPELCO’ column having stationary phase SPB-5 (SE-54); helium is employed as carrier gas; isothermal conditions are maintained with subsequent heating from \( T_{\text{min}} \) = 70 °C to \( T_{\text{max}} \) = 280 °C. Finally, the column is kept in isothermal conditions until elution is completed.

The mass-spectrometer employs ionization method involving electronic impact; the energy of ionization electrons: 70 eV; the temperature of the ionization chamber: 230 °C; masses are registered in the interval 33 – 400 a.m.u.; electron spectrum sweep: 0.4 sec.

The density of crude oil studied was defined according to ASTM D 1298.

Results and Discussion

The variation in the contents of petroporphyrins and organic acids was studied for the crude oil samples, which were obtained from Nos. 3063 and 6111 wells eleven and twenty-two months, respectively, after the Netrol and NINKA system injection. The results obtained are listed in Table 1.

The variation in the contents of vanadyl porphyrin complexes and of organic acids might be due to the effect of both systems.

As is seen from the data presented in Table 1 and Fig. 1, the vanadyl porphyrin content has increased in the crude oil samples collected from No. 3063 well eleven months after the Netrol system injection, while that of the samples collected twenty-two months after the Netrol system injection has remained practically the same. Evidently, the vanadyl porphyrin content of the crude oil samples obtained from Nos. 6111 and 1073 wells is unaffected by the NINKA system injection. It can be seen that the nickel porphyrin content remains practically unaffected by the Netrol and NINKA system injection.

The data presented in Table 1 and Fig. 2 suggests that the organic acid content has decreased by about half one month after the Netrol system injection. However, the organic acid content is found to increase by about 85 % (rel.) eleven months after
### Table 1. Petroporphyrin and organic acid contents of crude oil from Usinskoye field

<table>
<thead>
<tr>
<th>Well No.</th>
<th>Date of sampling</th>
<th>EOR technologies</th>
<th>Petroporphyrin content, nmole/g</th>
<th>Content, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>nickel</td>
<td>vanadyl</td>
</tr>
<tr>
<td>3000</td>
<td>02.2007</td>
<td>-</td>
<td>42.8</td>
<td>198.4</td>
</tr>
<tr>
<td>3063</td>
<td>02.2007</td>
<td>Netrol</td>
<td>31.3</td>
<td>135.1</td>
</tr>
<tr>
<td>3063</td>
<td>12.2007</td>
<td>Netrol</td>
<td>48.5</td>
<td>138.7</td>
</tr>
<tr>
<td>3063</td>
<td>11.2008</td>
<td>Netrol</td>
<td>35.4</td>
<td>168.0</td>
</tr>
<tr>
<td>2983</td>
<td>02.2007</td>
<td>-</td>
<td>31.2</td>
<td>185.4</td>
</tr>
<tr>
<td>6111</td>
<td>02.2007</td>
<td>NINKA</td>
<td>37.5</td>
<td>183.4</td>
</tr>
<tr>
<td>6111</td>
<td>12.2007</td>
<td>NINKA</td>
<td>23.4</td>
<td>182.5</td>
</tr>
<tr>
<td>6111</td>
<td>11.2008</td>
<td>NINKA</td>
<td>37.2</td>
<td>188.6</td>
</tr>
<tr>
<td>1073</td>
<td>12.2007</td>
<td>thermal-steam treatment</td>
<td>33.4</td>
<td>203.4</td>
</tr>
<tr>
<td>1073</td>
<td>11.2008</td>
<td>NINKA + thermal-steam treatment</td>
<td>34.7</td>
<td>192.3</td>
</tr>
</tbody>
</table>

![Fig. 1. Variation in the vanadyl porphyrin content of the crude oil samples collected from Nos. 3063 and 6111 wells in Usinskoye oil field with increasing time after the Netrol and NINKA system injection](image)
the Netrol system injection; a further increase in
the organic acid content (165 % rel.) is found to
occur twenty-two months after the injection.

The data also suggests that the organic acid
content of the oil samples collected from No. 6111
well first decreases and then gradually increases
up to 83 % (rel.) twenty-two months after the
NINKA system injection.

Using the method of liquid-adsorption
chromatography, we examined the effect of the
Netrol and NINKA system injection on the group
composition of studied oil, i.e. the contents of
saturated hydrocarbons (alkanes and naphthenes),
of aromatic hydrocarbons and of asphaltenes and
resins. The data listed in Table 2 suggests that
the crude oil samples collected from the wells of
Usinskoye field are characterized by high contents
of high-molecular heterogeneous components
(asphaltenes and resins). The contents of resins
and asphaltenes of the native oil samples are in
the range of 7.0 – 8.3 % (by mass) and 7.0 – 7.4 %
(by mass), respectively.

Fig. 3 through 5 illustrate variation in the
group composition of crude oil as a result of system
injection or thermal treatment of Nos. 3063, 6111
and 1073 wells (Netrol and NINKA systems and
thermal-steam treatment, respectively).

The content of resins and asphaltenes is
found to increase significantly (practically by a
factor of two) in the crude oil samples collected
from No. 3063 well relative to the native oil
samples obtained from No. 3000 well located in
the vicinity of the former. As is seen from Fig.
3, the content of saturated hydrocarbons (total
fraction \( T_{\text{b.p.}} \leq 200 ^\circ \text{C} \), oils included) has also
increased significantly due to a decrease in the
content of aromatic hydrocarbons. The oil fraction
in the distribution of saturated hydrocarbons is
found to grow due to the fraction \( T_{\text{b.p.}} \leq 200 ^\circ \text{C} \).
It is found, however, that the group composition
of the crude oil samples, which were collected
after prolonged time period had passed since the
injection, gradually returns to the original one.

As is seen from Fig. 4, the content of saturated
hydrocarbons (total fraction \( T_{\text{b.p.}} \leq 200 ^\circ \text{C} \), oils
included) of the crude oil samples collected from
No. 6111 well after the NINKA system injection
has also increased, which is due to a decrease in
the aromatic hydrocarbon content as is the case
with the Netrol system injection. However, the
content of resins and asphaltenes has changed
only insignificantly.

The distribution of saturated hydrocarbons
is found to change only insignificantly due to the
Table 2. The composition of the oil samples studied

<table>
<thead>
<tr>
<th>Well No. (date of sampling)</th>
<th>EOR technologies</th>
<th>Content, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fraction T_{b.p.} 200°C</td>
<td>Saturated HCs (Sat)</td>
</tr>
<tr>
<td>3000 (02.2007)</td>
<td>-</td>
<td>22.8</td>
</tr>
<tr>
<td>3063 (02.2007)</td>
<td>Netrol system</td>
<td>16.3</td>
</tr>
<tr>
<td>3063 (12.2007)</td>
<td>Netrol system</td>
<td>1.1</td>
</tr>
<tr>
<td>3063 (11.2008)</td>
<td>Netrol system</td>
<td>13.3</td>
</tr>
<tr>
<td>2983 (02.2007)</td>
<td>-</td>
<td>25.0</td>
</tr>
<tr>
<td>6111 (02.2007)</td>
<td>NINKA system</td>
<td>22.5</td>
</tr>
<tr>
<td>6111 (12.2007)</td>
<td>NINKA system</td>
<td>16.4</td>
</tr>
<tr>
<td>6111 (11.2008)</td>
<td>NINKA system</td>
<td>26.1</td>
</tr>
<tr>
<td>1073 (12.2007)</td>
<td>Thermal-steam treatment</td>
<td>4.8</td>
</tr>
<tr>
<td>1073 (11.2008)</td>
<td>NINKA system + thermal-steam treatment</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Fig. 3. Variation in the group composition of the crude oil samples collected from No. 3063 well after the Netrol system injection
growth of oil fraction (cf. an increase in the low-molecular fraction $T_{b.p.} \leq 200$ °C of the crude oil samples collected from the wells after the Netrol system injection).

A decrease in the total content of asphaltenes and resins (mostly at the expense of resins) and in the density of crude oil was observed for the crude oil samples collected from No. 1073 well after the NINKA system injection in combination with thermal-heat treatment (Fig. 5).

Moreover, the use of thermal-heat treatment in combination with the NINKA composition injection was found to cause an increase in the contents of saturated and aromatic hydrocarbons (total HCs) of the crude oil samples collected from No. 1073 well.

Using gas chromatography-mass spectrometry, the individual composition of hydrocarbons of the crude oil samples collected from No. 1073 well after the NINKA system injection was examined; the evidence obtained was analyzed. The results presented in Fig. 6 suggest that a sharp increase occurs in the contents of cyclic aliphatic compounds (pentacyclic triterpanes) and aromatic hydrocarbons (naphthalenes, phenanthrenes and triaromatic steroids). It is also found that among the aromatic compounds grows the fraction of structures having a large number of cycles in the molecule and among n-alkanes – the fraction of C$_{21}$-C$_{33}$ homologs, the concentration of alkyl benzene hydrocarbons remaining the same (0.7 %).

The relative contents of some homologs in the naphthalene-phenanthrene mixture are found to change. Thus the relative content of structures having a great number of alkyl substituents, i.e. tetramethyl naphthalenes and tetramethyl phenanthrenes (designated as TeMN and TeMP, respectively), is found to grow as was the case with alkanes, while the relative content of low-molecular structures, i.e. mono, di- and trimethyl naphthalenes (designated as MN, DMN and TMN, respectively), phenanthrene and methyl phenanthrenes (designated as P and MP, respectively), is found to decrease (Fig. 7).

Thus, the application of oil displacement systems for the recovery of crude oils having high contents of resins and low contents of saturated hydrocarbons would cause the resin content to decrease with resultant reduction in
the density of recovered crude oil. The contents of cyclic and aromatic hydrocarbons are found to increase; the fraction of structures containing a large number of condensed cycles also increases; among the aromatic hydrocarbons grows the fraction of high-molecular bi- and tri-arenes.

The above changes might be due to the distribution equilibrium of the oil-water system shifting towards the water phase. Thus owing to the system injection, resins, in particular, organic acids, vanadyl porphyrin complexes, low-molecular n-alkanes and naphthalenes, would become soluble in the water phase, which enhances the solution power of the latter phase with respect to the above compounds. In the course of time the solution power of the water phase grows less; as a consequence, the oil composition would return gradually to that of native oil.

The alkane content is found to decrease significantly in the crude oil samples collected from No. 3063 well eleven months after the Netrol system injection; among the aromatic hydrocarbons increases the fraction of naphthalene and phenanthrene structures (Fig. 8).

The above variations in the group composition and properties of crude oil are found to result from the application of methods and technologies for enhanced oil recovery. It can thus be concluded that the parameters analyzed can serve as criteria of treatment effectiveness; besides, these might help determine the time of operation of oil displacement systems and gel-forming compositions.

**Conclusions**

1. It is found that the NINKA system injection causes an increase in the hydrocarbon
As a result of the NINKA system injection, the content of resins and asphaltenes and oil density are found to decrease relative to the native oil.

3. The content of vanadyl porphyrins of crude oil studied is found to be unaffected by the NINKA system injection, while the content of organic acids would first decrease as a result of treatment to finally return to the initial value.

4. As a result of the NINKA and Netrol system injection, an increase is observed in the contents of cyclic and aromatic compounds, which have high portions of condensed cycles and high-molecular bi- and tri-arenes, respectively.

5. It is found that the Netrol system injection results in about a two-fold increase in the contents of resins and asphaltenes and saturated hydrocarbons (total fraction T_{b,p.} \leq 200 \degree C, oils included) due to a decrease in the aromatic hydrocarbon content.

6. The results obtained can be used to develop effectiveness criteria for oil displacement systems studied and to determine the operation time of the same systems under real oil production conditions.

References


Влияние воздействия нефтевытесняющих композиций на состав извлекаемой нефти

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Изучено влияние методов повышения нефтеотдачи на состав и свойства извлекаемой тяжелой высокосмолистой нефти Усинского месторождения (Республика Коми). Установлено, что под действием композиции Нетрол в нефти произошло увеличение содержания насыщенных углеводородов и смолисто-асфальтеновых веществ, за счет снижения содержания ароматических углеводородов. В результате воздействия композиции НИНКА также возросло содержание насыщенных углеводородов, но снизилось содержание смолисто-асфальтеновых веществ. Комплексное воздействие пара и композиции НИНКА привело к возрастанию содержания насыщенных и ароматических углеводородов, снижению плотности нефти.

Ключевые слова: тяжелые высокосмолистые нефти; технологии добычи; нефтевытесняющие композиции; насыщенные и ароматические углеводороды; органические кислоты; порфирины; групповой состав.