Hydrodynamic modeling of thermochemical treatment of low permeable kerogen-containing reservoirs

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Abstract. The work is devoted to the effectiveness analysis of thermochemical method of intensifying the hydrocarbons inflow using binary mixtures based on ammonium nitrate in the development of low-permeability reservoirs of unconventional hydrocarbons represented by petroleum-derived kerogen-bearing rocks. The concept of the research is aimed at determining the principles of treating kerogen-bearing layers and the creation of new scientific, methodological and technological solutions to increase the efficiency of developing deposits of these unconventional hydrocarbon reserves. Some properties of oil source formations located on the territory of the Russian Federation are generalized and structured. The results of investigations of the thermal treatment on rocks of the Bazhenov formation are generalized.

The authors present the principles of mathematical modeling of thermal and chemical processes, allowing to take into account the geological and hydrodynamic features of kerogen-containing rocks. We have described a mathematical model of the thermogas chemical treatment with the use of binary mixtures. The calculation results of the treating the field with highly viscous oil are given.

Based on the calculation results of thermal-gas-chemical treatment (TGCT) of low-permeable reservoir with highly viscous oil, a positive effect was obtained. Therefore, the authors conclude that the TGCT method, along with the search for other methods for the development of kerogen-containing reservoirs, can be considered promising and possibly more optimal than the thermal and chemical methods used.

Keywords: unconventional sources of hydrocarbons, kerogen, kerogen-containing rocks, thermochemical methods, mathematical modeling, generation of hydrocarbons


Specific strata, now called the Bazhenov formation, have been known for almost 60 years – in 1959 they were mentioned by F.G. Gurari in relation to the Priobsky field, geographically linked to the Bazhenovo-Sargatsky district of the Omsk region. At present, about 70 fields in Russia are referred to as oil and gas source in the Bazhenov formation. The rocks of the stratum are geographically located in Western Siberia, occur at a depth of 2-3 thousand meters and have a thickness of 10 to 100 m. At the same time, these layers are characterized by a small amount of mobile oil, low reservoir properties, while possessing a rather high content of organic matter – kerogen (about 14%, according to (Deliya, 2015); 5-40% according to (Kuz‘min, 2015)), as well as abnormally high reservoir pressures, which are 1.5-2 times higher than normal levels of hydrostatic pressures (Tarasova, 2012) and temperatures which are in range of 100-134°C. The Bazhenov layers were considered an impermeable cap of more productive formations and were considered ineffective in terms of operation. In the past 20 years, in connection with the development of new technologies and the success of the development of “shale oil” (oil of low-permeable tight rocks) in the United States and tar sands in Canada, the development of Bazhenov formation layers is no longer considered unpromising. However, the complex geological structure, the pronounced inhomogeneity of layers with different mineral compositions, permeability (even impenetrable), makes each section essentially unique in terms of the choice of development method. The presence of irregular clay interlayers (mainly mixed formations of hydromica) gives a significant anisotropy of the layers, while the relationship between the clay content and the percentage of kerogen does not have a
correlation connection (Kuz’min, 2015). The complexity of the structure of the Bazhenov strata is also due to the presence of the so-called dual porosity – open porosity and fracture “filled” with free mobile hydrocarbons and anomalously low porosity of the kerogen matrix itself. Usually it is believed that the porosity and permeability of kerogen is so small that the matrix is usually assumed to be impenetrable. However, recent studies show the dependence of both the open porosity of the core and the porosity of kerogen on the thermal maturity of kerogen, which differs significantly in different areas (Gil’manov, 2015).

The deposits of the Bazhenov formation, which have kerogen in the solid structural matrix, are conventionally referred to the group of so-called unconventional fields and even combined into a general subgroup of shale oil fields. Although fundamentally, it is a completely different type of hydrocarbons (type of kerogen) than similarly called fields, for example in the USA. Only small values of reservoir parameters and development complexity are related to them.

Now a lot of theoretical studies are devoted to the study of “Russian shale oil” fields, although, of course, there is already a rather long history of interest in studying kerogen in Russia, while the following have been established. It is inefficient to extract hydrocarbons from these layers by conventional methods, but laboratory experiments show the ability to activate the generation of mobile hydrocarbons from solid kerogen under certain conditions: temperatures of about T = 300°C make it possible to start the generation mechanism, and at temperatures above T = 700°C we can expect generation mobile hydrocarbons are actually in real time.

It should be noted that it is extremely difficult to transfer laboratory techniques to the practice of developing real deposits. An important factor here is the diversity of the geological structure, occurrence conditions, reservoir conditions for various deposits containing kerogen. In addition to the Bazhenov formation, there are several oil source strata in Russia. In the northeast of the Siberian platform, the Kuonam formation is located, containing alternating marls and argillites with an organic matter content of 0.1-19.5% (Zueva, 2012). The oil resources of the Kuonam formation range from 700 million tons according to VNIGNI (2011) to 15,000 million tons according to SNIIGGiMS (2017). The most studied Domanic formation is located on a large area of the eastern part of the East European Platform, with a kerogen content of about 5%, on the territory of which about 10 oil fields were found with a total volume of recoverable oil reserves of about 27 million tons (Prischchepa et al., 2014). Mining is not conducted. In the regions of Ciscaucasia and the North Caucasus, the Khadum formation is widespread, which partially has oil source areas with an average organic content of about 2%. The sediment thickness varies from 25 to 90 m (Egoyan, 1969). According to the Rosneft company, the open oil reserves of the Khadum formation are estimated at about 11 million tons, and there is almost no production.

Also in Ciscaucasia, at the depths of over 5 km, the Kumskian horizon is located, containing sapropel organic matter in concentrations of 0.5-5% (Distanova, 2007). Oil accumulations of this formation are predicted in the Crimean-Caucasus region, including the Tuapse Trough, poorly studied from a geochemical point of view. The Pilengsky formation of the Miocene age, with a capacity of 100 to 500 m and more, is the main productive horizon on Northern Sakhalin (Gladenkov, 2002). In the south-east of the Siberian platform, the Malginsk formation of the Middle Riphean is widespread. The content of organic matter in rocks varies from 0.04 to 12.69%, the average value is 4.37% (Dakhnova et al., 2013).

Table 1 shows the main properties of the described deposits – data on the location of formations, the type of rocks, approximate age, thickness of rocks, reservoir temperature and fraction of organic matter. Creating an effective method for extracting hydrocarbons from the formations described is more associated with the ability to activate the generation of mobile hydrocarbon fractions from the kerogen matrix directly in the formation.

A lot of theoretical and experimental works are devoted to the issue of kerogen hydrocarbons generation. The authors note that, in addition to elevated temperature, other factors are of great importance in order to achieve the process of in-situ conversion of kerogen to mobile hydrocarbons: the presence of cracks in the structure of the pore space, providing migration paths of the resulting decomposition products of kerogen (Korovin et al., 2014), the presence of catalysts, uniaxial geostatic pressure (Nesterov et al., 1993), water (Vorob’ev et al., 2007), hydrogen (Kayukova et al., 2011), the mineral component of the rock (Kokorev, 2010), and others.

Most researchers agree on the application of thermal methods of exposure to kerogen-containing rocks. Summarizing the results of studies of thermal effects on kerogen-containing rocks, it is necessary to indicate the following intra-layer processes revealed: the appearance of mobility of the bituminous components of fluids (viscosity reduction), which initially saturate the formation; generation of additional mobile hydrocarbons from the kerogen matrix of the rock, as well as the associated increase in porosity and the formation of additional fracturing.

The intensity of these processes depends not only on the thermobaric state of the reservoir system, but also on a number of particular factors that individualize a
particular area, for example, the presence of zones of anomalous cuts (alternating layers), the composition of the skeleton of the rock (the ratio of bituminous mudstones and sandy-aleurite layers, dolomitized sandstones, shale, etc.), the presence in the pore space of bound water. Difficulties in the study of fields are due to the fragility of the rocks, the destruction of the core during selection, and the change in reservoir properties under non-reservoir conditions. The question of the kinetics of transition of a kerogen to a mobile state also remains an urgent issue.

The largest number of experiments is devoted to pyrolytic decomposition (Rock-Eval method), which makes it possible to determine the yield of various components at a certain temperature level: at 100°C free gases are emitted from C1 to C4, at a temperature of 300°C the first peak S1 – characterizes the transition in the gas phase of liquid hydrocarbons C5-C7 and part of asphaltene, the second peak of S2 is recorded at T = 600-850°C with the release of tar-asphaltene substances and kerogen, the following peaks S3 and S4 correspond to the release of CO and CO₂ due to combustion of the residual th carbon. In this case, it is the peak S1 that characterizes the fraction of kerogen that has passed into the mobile state, and S2 – the part that remained in the solid state (unrealized potential). The sum S1+S2 is actually called the generation potential and reflects the maturing property of source rocks from various fields. On the basis of this technique, the source rocks are classified according to generation ability. However, using this method it is impossible to obtain dynamic links between process parameters. In this paper (Gaiduk, 2009), a new approach to the description of kinetics was proposed, which allows calculating the thermodynamic characteristics of not individual components, but kerogen in general, and to calculate the thermodynamics of any stages of kerogen catagenesis on this basis.

Table 1. Basic oil source formations of Russia

<table>
<thead>
<tr>
<th>Formation</th>
<th>Location</th>
<th>Type of rocks</th>
<th>Age</th>
<th>Thickness, m</th>
<th>Area, km²</th>
<th>Fraction C.food</th>
<th>Temperature of format.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bazhenov</td>
<td>Western Siberia</td>
<td>Carbonate-clay-siliceous deposits</td>
<td>Late Jurassic</td>
<td>20-60</td>
<td>&gt;1 mln</td>
<td>14%</td>
<td>80-140°C</td>
</tr>
<tr>
<td>Kumsk</td>
<td>Ciscaucasia</td>
<td>Marls, clays, bituminous shales containing large fish scales</td>
<td>Eocene</td>
<td>40-60</td>
<td>40-50 thous.</td>
<td>0,5-5%</td>
<td>82-100°C</td>
</tr>
<tr>
<td>Khadum</td>
<td>Ciscaucasia</td>
<td>Clays with interlayers of marls and siltstones</td>
<td>Oligocene</td>
<td>25-90</td>
<td>450 thous.</td>
<td>5%</td>
<td>40-180°C</td>
</tr>
<tr>
<td>Domanic</td>
<td>Eastern European part of Russia</td>
<td>Clay-carbonate rocks</td>
<td>Late Devonian</td>
<td>20-100</td>
<td>400 thous.</td>
<td>Domanicoids (0,5-5%), Domanicites (5-25%)</td>
<td>30 °C</td>
</tr>
<tr>
<td>Kuonam</td>
<td>East Siberia</td>
<td>Domanicites, calcareous-clay and calcareous-siliceous shales, marls, clay limestones</td>
<td>Early Cambrian</td>
<td>20-70</td>
<td>114 thous.</td>
<td>0,1-19%</td>
<td>n/d</td>
</tr>
<tr>
<td>Pilengsky</td>
<td>North Sakhalin</td>
<td>Fine interbedding of pelitomorphic siliceous and clay-siliceous rocks with interlayers of tuffs, sandstones and aleurolites</td>
<td>Miocene</td>
<td>100-500</td>
<td>20-30 thous.</td>
<td>0,3-2,9%</td>
<td>n/d</td>
</tr>
<tr>
<td>Malginsk</td>
<td>South-East of the Siberian platform</td>
<td>Variegated fine-limestone, turning into gray, sometimes bituminous limestone</td>
<td>Paleozoic</td>
<td>100-400</td>
<td>30-40 thous.</td>
<td>0,04-12,69%</td>
<td>n/d</td>
</tr>
</tbody>
</table>
and frequently used function that relates porosity and permeability is the Kozeni-Karman formula.

However, the peculiarity of kerogen-containing rocks in the form of their low permeability and tendency to cracking under thermal influence does not allow the latter dependence to be applied, but requires further clarification of the method of describing a significant increase in permeability with a slight change in porosity. At small porosity values, the linear Kozeni-Karman function can be replaced by the exponential dependence of the permeability drop on porosity. For Bazhenov formations, the study of core material showed the irregularity of the functional dependence of porosity – permeability (Kuz’mín, 2015).

The lack of correlation due to a wide range of fractional composition, bulk density and chaotic fracturing and cavernosity. The choice of the method of influence on the kerogen-bearing strata currently remains open. The works (Dieva, 2015; Kravchenko et al., 2016; Kravchenko et al., 2018) gave a detailed review of approaches to the practical implementation of development projects for fields containing kerogen. The authors’ work showed that the temperature levels required for the active generation of hydrocarbons from the kerogen matrix can be efficiently and safely for mining equipment obtained by decomposing solutions of explosives in the formation. The fundamentals of the thermogas-chemical exposure technology based on aqueous solutions of explosives were developed more than 15 years ago (Aleksandrov et al., 2004) and have been significantly modified recently (Alexandrov et al., 2016; Vershinin et al., 2016). The essence of the thermogas-chemical exposure technology (TCET) method is to inject a solution of explosives into the formation and stimulate explosives to decompose. The authors suggested using for this purpose a saturated aqueous solution of a binary mixture (BM) – ammonium nitrate mixed with sodium nitrite. Schematically, the interaction reaction solutions can be represented as follows (Mel’nikov, 1987):

\[
\text{NH}_4\text{NO}_3 + \text{NaNO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + \text{NaNO}_3 + Q_1. \quad (1)
\]

As a result of this reaction, heat of 4688 kJ per kilogram of nitrate is released. At temperatures above 200°C in the presence of chlorine ions, thermal decomposition of nitrate occurs:

\[
\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2 + 2\text{H}_2\text{O} + 0.5\text{O}_2 + Q_2. \quad (2)
\]

In reaction (2), 2650 kJ are released per kilogram of nitrate (Mel’nikov, 1987). The released oxygen and heat initiates the oxidation of residual oil in the reservoir:

\[
\text{C}_n\text{H}_{2n+2} \cdot 1/2\text{O}_2 \rightarrow \text{C}_n\text{O}_2 + \text{CO}_2 + 2\text{H}_2\text{O} + Q_3. \quad (3)
\]

Reaction (3) also comes with the release of heat, which is estimated at 2380 kJ per 1 kg of nitre throughout the chain of reactions (Aleksandrov et al., 2007). The total heat dissipation as a result of all reactions of solutions of a binary mixture lies in the range from 4688 to 5030 kJ of heat per kilogram of nitrate.

The temperature reached in the reaction zone will depend on the concentration of nitrate, residual oil saturation, injection rate and external conditions. Fig. 1 shows the results of laboratory studies of temperatures achieved by the decomposition of a binary mixture at different concentrations of explosives in water (made in JSC GosNII CRYSTAL). Numerical simulation of the process of heating the reservoir in the near-wellbore region with different BS injection volumes showed that the temperatures reached depend on the concentration of nitrate in the BM, the water saturation of the solution, residual oil saturation, injection rate and external conditions. Fig. 2 shows the calculated temperature levels at different distances from the well, depending on the volume of injection of explosives (in tons).

As follows from Fig. 1 and 2, the injection of explosives allows reaching reservoir temperatures sufficient to initiate the reaction of decomposition of kerogen. By varying the salt content in the solution and the volumes of BM injected solutions, it is possible to achieve the required temperature levels in the near-wellbore region.

BM injection technology seems to be the safest compared to other explosives by regulating the energy component of the decomposition of ammonium nitrate by selecting the appropriate concentration of explosives in an aqueous solution and special inhibitors of chemical reactions. The technique is successfully used in oil fields at a late stage of development. Details of the description of the injection method based on ammonium nitrate mixtures, the decomposition of which in the reservoir leads to an increase in temperature due to the exothermic reaction of decomposition of explosives, reduced fluid viscosity and enhanced oil recovery are described in detail in (Volpin et al., 2014; Kravchenko et al., 2018; Vershinin et al., 2018). This technology allows creating in the reservoir a zone of high temperatures of up to 500°C, actually necessary for the generation of liquid hydrocarbons from kerogen.

The work (Kravchenko et al., 2016) substantiates the possibility of the effective application of the thermogas-chemical effect on the kerogen-bearing rocks of the Bazhenov formation.

At this stage of the theoretical study, the authors took into account the diversity of laboratory and field experiments with kerogen, core materials of kerogen-containing formations and created a mathematical model that allows one to numerically evaluate the nature of such an impact on unconventional low-permeable reservoirs, including kerogen-containing. The model allows to take into account the generation of heat in the zone of explosive decomposition, the change of thermobaric...
parameters, the transformation of the reservoir itself due to changes in its structure, including the decomposition of the solid phase (kerogen) with the release of additional mobile hydrocarbons.

Fig. 3 schematically shows an element of the computational three-dimensional region that simulates the region of a saturated reservoir bounded by an impermeable roof and bottom. The figure shows the areas of sequential injection of various fractions of working fluids in the process of organizing the TCET and the formation of the reaction zone during the decomposition of explosives.

Mathematical modeling of TCET processes is carried out in several stages. At the first stage of modeling this process, the task of pumping the necessary volumes of reacting and buffer substances is calculated according to the rules of GIS technology at a particular field and candidate well. Analysis of the field saturation distribution fields allows setting the time and place for the thinning of the buffer water zone separating the reacting substances and, accordingly, the location of the reaction zone of chemicals and the thickness of the interaction zone of the reacting substances (Fig. 3).

Hereafter are some of the results of calculations describing the organization of TCET in a 25-meter-thick cylindrical reservoir to the regulations that involve the injection of a binary mixture with a volume of $20 \text{ m}^3$ and the following squeezing water in a volume of $170 \text{ m}^3$.

Fig. 1. The level of temperature increase during the decomposition of $\text{BM NH}_4\text{NO}_3/\text{NaNO}_2$

Fig. 2. Estimated levels of temperatures reached in the bottomhole zone at various volumes of $\text{BM NH}_4\text{NO}_3/\text{NaNO}_2$ injection

Fig. 3. Diagram of the computational domain in the well bore zone with sequential supply of reagents and formation of the reaction zone
Under these conditions, the distance of the reaction zone from the wellbore is 2.5 meters. The next stage of the simulation describes the development process of this reaction, in the form of an increase in pressure and temperature in a narrow region surrounding the well and remote from it at a distance calculated in the previous step. The intensity of the reaction, which determines the levels of arising temperatures and pressures, depends on the injection volumes of the reactants, as well as the concentration of salts in their composition.

Studies have shown that when using solutions with a salt concentration of about 10%, the maximum temperature in the reaction zone does not rise above 100°C, and the use of salts with a concentration of about 60% leads to an increase in temperature above 400°C, while pressure jumps due to decomposition of BM and gas emission reaches 800 atm in the reaction zone, the intensity of the wave decreases as it “spreads” from the reaction zone. Fig. 4 shows a graph of the time pressure changes at the well when the “explosive” pressure wave reaches the well. When the reaction distance from the well is 2.5 meters (at 60% concentration of explosives), a pressure pulse of 440 atm comes to the face after about 2.5 hours.

At the third stage of modeling, the process of production from a heated reservoir is calculated, changes in temperature distribution, pressure in the well bottom zone, advance of phase fronts, changes in porosity and permeability are tracked. In the zones of the reservoir, where the pressure rose above 300 atm changed porosity and permeability caused by the formation of a system of small cracks. The propagation of the thermal front from the zone of interaction of the reacting substances of the TCET showed heating of the formation above 80°C to a depth of 10 meters from the well during the week.

**Conclusions**

The TCET methods tested on conventional fields over the past 10 years have shown a good effect in the form of a continuous increase in inflows at fields that are at a late stage of development. Depending on the volume of injected explosives and the concentration of solid explosives in an aqueous solution, it is possible to change the thermodynamic parameters (temperature and pressure) in the reaction zone, due to a change in the overall level of energy release. The use of reaction retarders supplied before or together with an aqueous solution of explosives, allows delaying the development of the reaction for the required period of time necessary for pushing the reaction zone from the wellbore by feeding volumes of squeezing liquids, which makes it possible to carry out the process in a safe mode for the well.

Increasing the concentration of explosives (over 60%) in an aqueous solution makes it possible to obtain temperatures above 400 °C in the reaction zone, which are sufficient to activate the process of generating additional hydrocarbons from kerogen, which indicates the promising application of the TCET method for kerogen-containing fields.

![Fig. 4. Dynamics of pressure change at the bottom of the well since the beginning of the BM decomposition reaction](image-url)
The process of generation of mobile hydrocarbons from kerogen in the model is initiated when the temperature in the reservoir reaches not less than 300°C, however, in the absence of specific field data on the decomposition of kerogen, this process was not considered in the calculation, but the possibility of its generation under various test protocols was evaluated.

As it is known in 2015, the “Shpilman Scientific and Analytical Center for the Rational Use of Subsoil Resources” together with the Ministry of Environment announced the creation of a scientific testing ground “Bazhenovsky “in Surgut region from the Khanty-Mansysk district (Kuz’min, 2015). The announced list of works concerns laboratory analysis of core material and geophysical research. According to the results of work, the values of porosities (5-30%) and permeabilities (0.001-1 mD) for various sections are already presented.

The research results could be the basis for the creation of adapted mathematical models, based on which it is possible to optimize the development of kerogen-containing formations.

References


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Hydrodynamic modeling...

M.N. Kravchenko, N.N. Dieva, A.N. Lishchuk et al.

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