

## Geochemical Modeling with the Use of Vertical and Horizontal Relative Concentrations of Oil Compounds for the Heavy Oil Fields

Artyom E. Chemodanov<sup>1\*</sup>, Robert R. Akhmadullin<sup>2</sup>, Vladislav A. Sudakov<sup>1</sup>, Sergey A. Usmanov<sup>1</sup>, and Rinat K. Khayrtdinov<sup>1</sup>

<sup>1</sup> Institute of Geology and Petroleum Technology, Kazan (Volga Region) Federal University, Russia

<sup>2</sup> PAO "Tatneft", Russia

### ABSTRACT

The purpose of this study is the detection of lateral and vertical gradients of relative concentrations of compounds presented in oil. In addition, the detection allows us to assess potential drainage zones in a reservoir during the reservoir production by steam injection. In this paper, a new method for monitoring of steam chamber development in a 2D model was created and tested.

The methodology is used to consider the total hydrocarbon fraction. In addition, the total hydrocarbon fraction has been isolated from core extracts and has been analyzed by GCMS method (TIC) for detection of various compounds and assessment of lateral and vertical gradients of their concentration in lateral.

It has been found out that the ratio of 4- and 1-methyldibenzothiophenes (MDBT) changes in lateral and in vertical directions. These changes are caused by biodegradation of organic matter. Also laboratory research shows that 1-MDBT/4-MDBT ratio in native reservoir rocks is stable under high temperatures and pressures and this can be easily measured by GC-MS. This measurement will allow assessment of location and direction of steam chamber propagation.

In a recent work, the authors have developed a geochemical model which can be used for assessment of oil flow directions during the development of heavy oil fields by SAGD method.

**Keywords:** SAGD Modeling, Biodegradation of Oil, Beteroatomic Compounds, Isomers, Oil-water Transition Zone

### INTRODUCTION

The development prospects of the oil industry have recently been linked to the development of deposits of heavy oil and natural bitumen. In the mid-1980s, Canada developed a Steam Assisted Gravity Drainage (SAGD) technology [1].

A large number of works have been published

[2-4] about the modeling of developing super viscous oil deposits using the SAGD method, but many of the parameters characterizing the nature of the reservoir and the basic properties of the oil have been simplified. This may cause significant differences in the model and the real object it describes, which will leads to an inaccurate

#### \*Corresponding author

Artyom E. Chemodanov  
Email: chemodanov41659@mail.ru  
Tel: +79 19633 6546  
Fax: +79 19633 6546

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prediction of the oil production process.

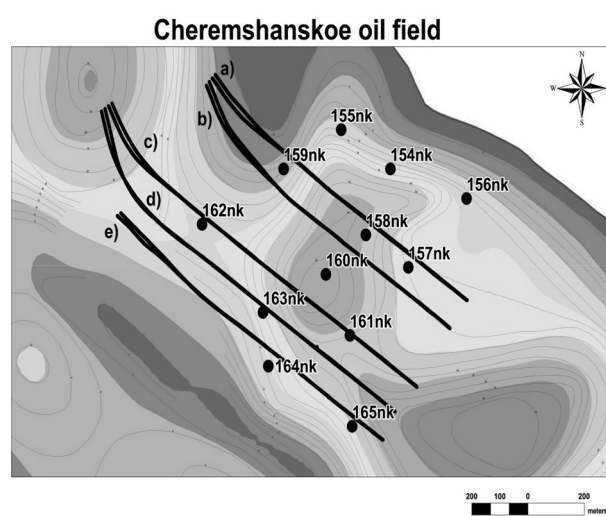
One promising solution to this problem is the geochemical modeling of the fields, based on the study of the composition zonation and the properties of the oil in the deposit. As we known, any oil contains a unique set of compounds; the ratio between them can both maintain constant values throughout the reservoir as well as show lateral and horizontal gradients. The zoning of the composition and properties of oil in shallow deposits are mainly associated with the biodegradation of organic compounds and is significantly different from the changes caused by physical processes such as washing out and fractionation. For example, the article [5] shows that hopanes, methyladamantanes do not have horizontal gradients by the content, while the concentration of mono-, di- and tri-aromatic hydrocarbons (including heteroatomic) decreases with depth. In [6] authors demonstrated that concentration of 6H-Farnesol in oil may be increased with depth. Specifying dependency of the distribution of any compounds over the whole field will certainly clarify the location and direction of the steam chamber by using GCMS analysis of the extracted oil.

Thus, the establishment of a method for monitoring the development of deposits by natural oil markers is a matter of urgency, which will make it possible to clarify existing patterns of deposits and improve their predictive capacity.

The purpose of this work is to identify the gradients of ratios of compound molecules and show their possible use for the development of super viscous oil deposits in the case of the Nizhne-Karmal'skoe anticline of the Cheremshanskoe oil field (Tatarstan, Russia), where the SAGD technology is currently being used.

## EXPERIMENTAL PROCEDURES

The research objects are core samples, selected from the 12 appraisal wells of the Nizhne-Karmal'skoe anticline of the Cheremshanskoe oil field (Figure 1). In addition, we analyzed 2 core samples after hydrothermal treatment and 5 samples of oil extracted by the SAGD method.



**Figure 1: Location of the appraisal and horizontal wells of the Nizhne-Karmal'skoe anticline of the Cheremshanskoe oil field.**

The results of the macro description of core show that the oil reservoir being studied has one layer in the entire field, but its depth and thickness vary greatly. The core samples were selected on the whole thickness of the productive reservoir, if possible at the same intervals. As a result, the number of core samples selected from the appraisal wells ranged from 3 to 6 per well, and the thickness of the sampling interval was 4-8 meters, depending on the thickness of the oil reservoir (Table 1). The upper and lower samples were selected as close as possible to the top and the base surface of the reservoir.

**Table 1: The number of core samples selected from the assessment wells.**

No.	Well	The depth of the oil reservoir, m			Number of samples
		Top	Base surface	Thickness	
1	154	131.5	154.1	22.6	4
2	155	145.4	156.2	10.8	3
3	156	129.6	158.2	28.6	4
4	157	124.4	160.0	35.6	6
5	158	130.2	160.3	30.1	5
6	159	151.8	168.3	16.5	3
7	160	137.1	170.0	32.9	6
8	161	129.8	168.8	39.0	5
9	162	171.0	179.0	8.0	3
10	163	150.0	174.3	24.3	4
11	164	149.8	182.3	32.5	5
12	165	132.6	162.6	30.0	4
<b>Total</b>					<b>52</b>

The extraction of bitumen using chloroform was carried out using the Soxhlet extractor. The hydrocarbon fraction, containing saturated and aromatic hydrocarbons, provided using a method of liquid-absorbed chromatography on the

siliceous gel (0.25-0.5 mm fraction). Petroleum-ether was used as a movable phase.

The hydrocarbon fraction of bitumen and oil was examined on the gas chromatography/mass spectrometer system. The gas chromatography/mass spectrometer system included the gas chromatograph "Chromatech-Crystal 5000" with a mass-selective ISQ detector. The Xcalibur software has been used for processing the results. The chromatograph is fitted with a capillary column, 30 m long, with a diameter of 0.25 mm. The speed of the flow of carrier gas (helium)-1 mL/min. The injection temperature is 310 °C. The temperature program of the thermostat is a rise from 100 to 150 °C at a speed of 3 °C/min, from 150 to 300 °C at a speed of 12 °C/min followed by its isotherm to the end of the analysis. Electron energy-70 eV, temperature of ion source-250 °C. The compounds have been identified through the electronic library of the NIST spectra and according to the data of the literary sources.

The hydrothermal processing of core samples was performed in the digestion bomb Parr Instruments 4560 (USA), with a volume of 300 cm<sup>3</sup> with mixing under the following conditions: Initial pressure 3 bar, operation pressure 17 bar, operational temperature 200 °C. The duration of the operational process was 6 hours. The core relative water content was 10%.

## RESULTS AND DISCUSSION

### Search for Compounds with Concentration Gradients

The chromatography-mass-spectrometric analysis of hydrocarbon fractions shows the absence of normal alkanes and the dominance of isoprenoid hydrocarbons in all samples (Table 2).

**Table 2: Results of the GCMS (gas chromatography-mass spectrometry) analysis of hydrocarbon fractions of Bitumen.**

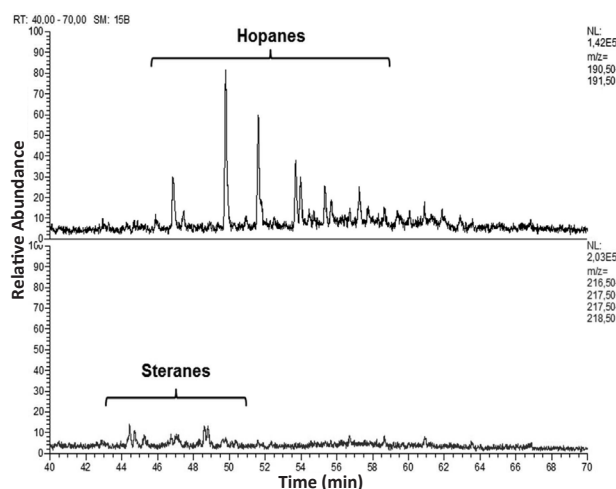
Compound	m/z	Presence (+/-)	Note
N-alkanes	TIC *, 85	-	Not found even in trace amounts
Isoprenoid alkanes	TIC, 85	+	The contents vary between 60 and 90% rel. (78% on average for all samples)
Monoaromatic hydrocarbons	TIC, 91, 133	+	The content varies between 2 and 20% rel. (10% on average for all samples)
Naphthalene	128	-	-
Monomethylnaphtalene	142	-	-
Dimethylnaphtalene	156	-	-
Trimethylnaphtalene	170	+	-
Tetramethylnaphtalene	184	+	-
Steranes	217	+	The main sterane and hopane geochemical coefficients are the same for all specimens
Hopanes	191	+	

\* TIC-Total Ion Current

The absence of n-alkanes in the core sample indicates the degradation of organic matters. There exist two classical scales of oil biodegradation, namely Peters-Moldovan (PM) [7] and Wenger [8] scales, based on which ones can assess the approximate depth of biological destruction of organic matters. Both scales were used for the assessment of the availability of n-alkanes, isoprenoids, steranes, and hopanes. The Wenger scale, unlike the PM scale, also includes the identification of di- and tri-aromatic compounds. Table 2 shows that, apart from the lack of n-alkanes, which we can observe on the total ion current, there are no C<sub>0</sub>-C<sub>2</sub>-Naphtalenes in the specimens studied, although C<sub>3</sub>-and C<sub>4</sub>-Naphtalenes are still identifiable. It is also worth noting that the presence of monoaromatic hydrocarbons, hopanes, and will be mentioned. On the basis of the results of the gas chromatography/mass analysis, we concluded that organic matters in the specimens are moderately biodegraded on the PM scale (4-5 units) or heavily biodegraded on the Wenger scale (3 units).

It is necessary to determine which components

surviving in the biodegradable environment are characterized by gradients of relative concentrations throughout the deposit. Relative concentrations of isoalkanes and aromatic hydrocarbons do not have any patterns in the distribution of the prospect. Vertical and lateral gradients of hopane and sterane geochemical factors of are also not observed. For example, the value of the coefficient 22S/(22S + 22R) is stable [9], almost identical for all specimens, and is 0.58-0.61 (Figure 2).



**Figure 2: GCMS chromatograms for steranes and hopanes (m/z = 191, 217+218).**

Heteroatomic compounds are quite resistant to the processes of degradation [10]. Two of these compounds, which represent in all studied samples, are 1- and 4-methyldibenzothiophenes. In work [11] was shown that 4-methyldibenzothiophene (4-MDBT) was less resistant to degradation than 1-methyldibenzothiophene (1-MDBT) so that the ratio 1-MDBT/4-MDBT is an indirect indicator of the degree of degradation of organic matters. Figure 3 shows mass-chromatograms (by  $m/z = 198$ ) of two samples of the well No. 163 core, indicating the peaks of 1-MDBT and 4-MDBT.

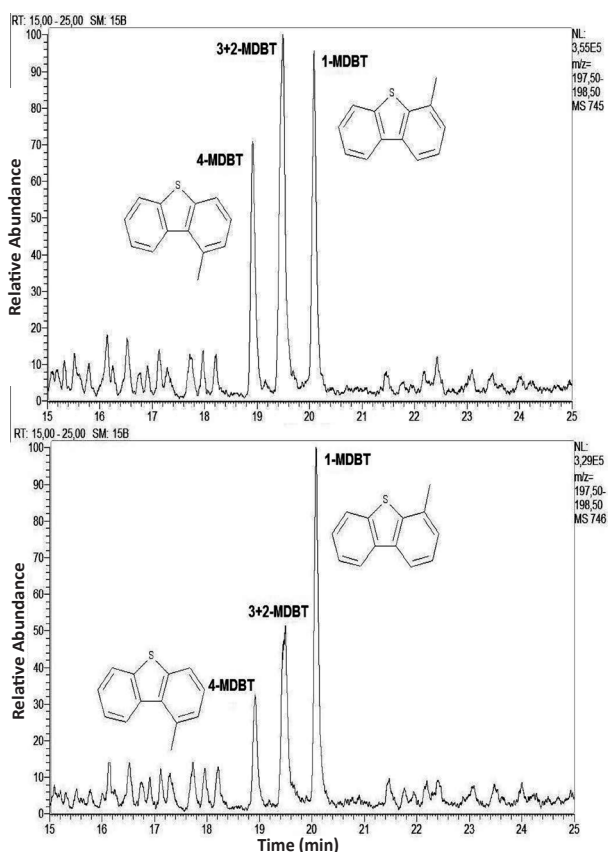


Figure 3: Mass-chromatograms ( $m/z = 198$ ) of various samples of the well No. 163.

### Construction of A Geochemical Model for The Distribution of Ratio 1-MDBT/4-MDBT

For all core samples, a ratio of 1-MDBT/4-MDBT, which varies in the range of 0.4-11.0 (Table 3), has

been defined. Average values of 1-MDBT/4-MDBT on wells lie between 0.6 and 9.4.

Table 3: Values of the 1-MDBT/4-MDBT ratio for kern samples from different wells.

Well	The depth of the productive layer, m	1-MDBT/4-MDBT ratio	
		The increase of the sampling depth	Average value of the well
154	131.5 – 154.1	0.9 – 0.9 – 1.9 – 2.1	1.5
155	145.4 – 156.2	8.0 – 9.2 – 11.0	9.4
156	129.6 – 158.2	1.3 – 1.3 – 2.5 – 0.4	1.4
157	124.4 – 160.0	0.5 – 0.7 – 0.6 – 0.7 – 0.7 – 1.6	0.8
158	130.2 – 160.3	0.6 – 0.7 – 0.9 – 0.7 – 1.8	0.9
159	151.8 – 168.3	3.3 – 2.8 – 2.7	2.9
160	137.1 – 170.0	0.6 – 0.7 – 0.6 – 0.6 – 0.9 – 2.2	0.9
161	129.8 – 168.8	0,6 – 0,5 – 0,8 – 0,9 – 0,4	0.6
162	171,0 – 179,0	1,2 – 5,3 – 8,7	5.1
163	150,0 – 174,3	1,0 – 1,2 – 1,1 – 2,8	1.5
164	149,8 – 182,3	0,9 – 1,1 – 1,1 – 2,6 – 2,2	1.6
165	132,6 – 162,6	0,7 – 0,9 – 3,5 – 3,7	2.2

According to the lateral distribution of the average ratios 1-MDBT/4-MDBT, the geochemical 2D models of the area of the deposit (Figure 4) were constructed using Schlumberger Petrel 2013 software. Zones with low values of 1-MDBT/4-MDBT are colored blue and dark blue, and the zones with a high ratio are yellow and red. It should be noted that we have a reasonably accurate model using data from six wells. Adding six more wells does not radically change the model which was built, but merely makes it more accurate.



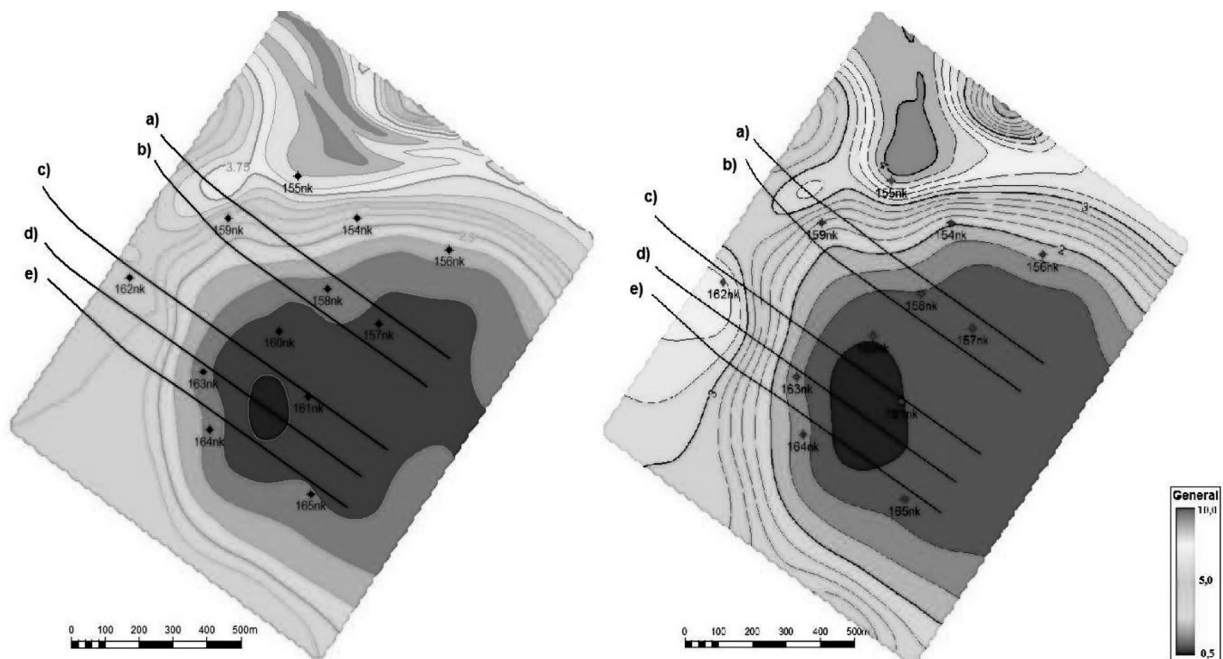


Figure 4: Lateral distribution of the average value of 1-MDBT/4-MDBT by area based on data for 6 wells (left) and 12 wells (right). The black lines indicated by the letters (a) to (e) are the horizontal extracting wells.

According to Table 3, the ratios 1-MDBT/4-MDBT can be quite different even for samples taken from the same well but from different depths. The vertical distribution of the ratios 1-MDBT/4-MDBT for some of the appraisal wells situated close to the production well is presented in Figure 5. In addition these wells have relatively low values of 1-MDBT/4-MDBT at the top of the productive layer. In the lower

part of the oil reservoir, there is a sharp increase in the ratio of isomers of methylbenzothiophenes: at a depth of 150 meters for wells 157, 158 and 160 and at a depth of 160 meters for wells of 160 and 163. It is important to note that this pattern is not characteristic for the well 161, as the entire thickness of its productive layer is low in the values of 1-MDBT/4-MDBT.

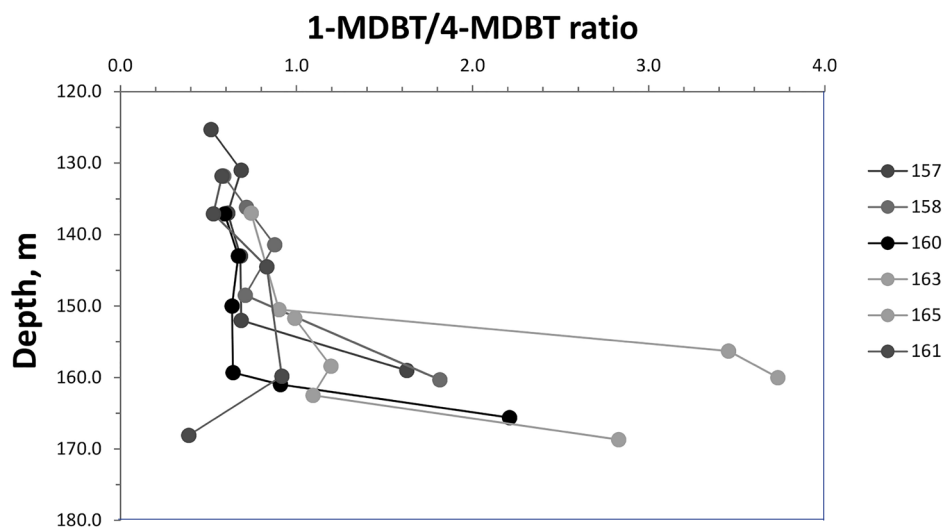


Figure 5: Vertical distribution of 1-MDBT/4-MDBT ratios for some appraisal wells.

The gradients obtained may be related to the presence of oil-water transition zone at a depth of 150-160 meters, where the most intensive biodegradation of organic matters occurs. As the depth of oil decreases, its biological decomposition is also beginning to be suspended. It is also worth noting that the indicator 1-MDBT/4-MDBT correlates with the thickness of the oil reservoir, which is exponential (Figure 6), due to the reduction in biological effects while reducing the thickness of the productive layer.

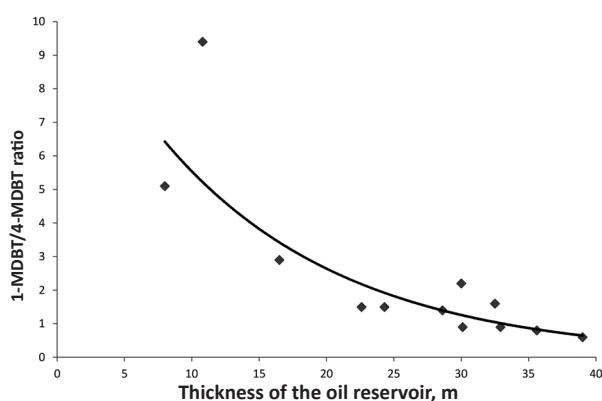


Figure 6: Dependence of average ratio 1-MDBT/4-MDBT of the wells from the thickness of the oil reservoir.

### Check of the Reliability of the Received Models

It is clear that the constructed models can assess the likely pathways of super viscous oil inflows by measuring the ratio of 1-MDBT/4-MDBT. However, some heteroatomic compounds may be destroyed in steam-heat processing conditions. For example, in the work [12], it was shown that thiophene is desulphurized even at lower temperatures, with the catalytic effect of the hematite contained in the rock. Afterwards, the impact of hydrothermal treatment on the ratio of isomers of methylthiophenes in super viscous oil extracted by SAGD technology need to be clarified for the correct application of the models received.

A laboratory modeling of reservoir conditions has been chosen as a tool to verify this influence. It is covered by a wide range of publications [13-14]. Two core samples with different values of 1-MDBT/4-MDBT were placed in an autoclave in conditions more stringent than those of the SAGD conditions (they are given in the experimental part of the article). After hydrothermal treatment, a hydrocarbon fraction was identified and analyzed on the gas chromatography/mass spectrometer. The results of the GHMS analysis showed almost identical ratios of 1-MDBT/4-MDBT in the processed specimens compared to the original. On the basis of the experiment, it has been established that hydrothermal processing of the core does not affect the distribution of isomers of methylthiophenes as part of its organic matter. In addition, a change in the ratio 1-MDBT/4-MDBT in the super viscous oil produced by the SAGD method, seemed to be negligible.

In order to suggest possible ways of inflow of oil to the horizontal wells, samples of the oil from the horizontal wells shown in Figure 1 were marked from (a) to (e) were analyzed. The molecular composition of oil hydrocarbon fractions, according to HMS analysis, showed the same components as found in the core samples (Table 2). However, the 1-MDBT/4-MDBT ratios for samples of extracted oil from the horizontal wells showed the results presented in Table 4.

Table 4: The results of the definition of the ratio 1-MDBT/4-MDBT in the specimens of the oil extracted using the SAGD technology.

Well	1-MDBT/4-MDBT
a)	0.6
b)	0.7
c)	0.5
d)	1.6
e)	0.6

The ratio 1-MDBT/4-MDBT for specimens (a), (b), (c) and (e) is roughly the same, 0.5-0.7, which corresponds to the blue zone on the lateral distribution. In addition, for these horizontal wells, it can be excluded that the shift of the steam camera will be down horizontally. For sample (d) the 1-MDBT/4-MDBT ratio is 1.6, and thereby the ratio indicates that there are inflows of super viscous oil to the production well from the lower part of the productive layer (from a depth of 150-160 meters).

## CONCLUSIONS

In this paper, the level of biodegradation of organic matter in the Nizhne-Karmal'skoe anticline of the Cheremshanskoe oil field was established. We found the presence of horizontal and lateral gradients of the ratio of methyl dibenzothiophenes in the organic matter of the oil reservoir. Moreover, the stability of this ratio in conditions of SAGD process was shown. The presence of these gradients is determined by the depth of the occurrence, the thickness of the oil reservoir, and (by paying attention to) the location of the appraisal wells. Within the developed model, it has been shown that the molecular composition of produced super viscous oil suggests possible ways of influx in the development of the deposits by the SAGD method.

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## NOMENCLATURES

CG-MS	: Gas Chromatography-Mass Spectrometry
COF	: Cheremshanskoe Oil Field
MDBT	: Methyl dibenzothiophenes
SAGD	: Steam-Assisted Gravity Drainage
TIC	: Total Ion Current

## REFERENCES

1. Butler R. "Horizontal Wells and Steam-assisted Gravity Drainage," *The Canadian Journal of Chemical Engineering*, **1991**, 69(4), 819-824.
2. Khisamov R., "The Analytical Model for Development of Heavy Oil Deposit by Steam-assisted Gravity Drainage Method," *Neftyanoe Khozyaystvo-Oil Industry*, **2015**, 2, 62-64.
3. Akin S., "Mathematical Modeling of Steam Assisted Gravity Drainage," *SPE Reservoir Evaluation and Engineering*, **2005**, 8, 372-376.
4. Alali N., Reza M., and Jabbari H., "A New Semi-analytical Modeling of Steam-assisted Gravity Drainage in Heavy Oil Reservoirs," *Journal of Petroleum Science and Engineering*, **2009**, 69, 261-270
5. Bennett B. and Adams J. "The Controls on the Composition of Biodegraded Oils in the Deep Subsurface-Part 3," The impact of microorganism distribution on petroleum geochemical gradients in *Biodegraded Petroleum Reservoirs Organic Geochemistry*, **2013**, 56, 94-105.
6. Chemodanov A. E., Sudakov V. A., Usmanov S. A., and Ahmadullin R. R., "Application of Geochemical Model for Monitoring the Superviscous Oil Deposits Development by the Thermal Steam Methods," *Neftyanoe Khozyaystvo-Oil Industry*, **2017**, 9, 104-107.
7. Peters K. and Moldowan J., "The Biomarker



- Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments," Prentice Hall, Englewood Cliffs, NJ, **1993**.
8. Wenger L., Davis C., and Isaksen G., "Multiple Controls on Petroleum Biodegradation and Impact on Oil Quality," *SPE Reservoir Evaluation and Engineering*, **2002**, 5, 375-383
  9. Seifert Wolfgang K., "Application of Biological Marker Chemistry to Petroleum Exploration," *World Oil*, **1980**, 2, 425-438
  10. Peters K., Walters C., and Moldowan J., "The Biomarker Guide," Biomarkers and Isotopes in *Petroleum Exploration and Earth History*, Cambridge University Press, **2005**.
  11. Bennett B., Adams J., and Larter S., "Oil Fingerprinting for Production Allocation: Exploiting the Natural Variations in Fluid Properties Encountered in Heavy Oil and Oil Sand Reservoirs," *Frontiers + Innovation CSPG CSEG CWLS*, **2009**, 157-160
  12. Khalil M., Lee R., and Liu N., "Hematite Nanoparticles in Aquathermolysis: A Desulfurization Study of Thiophene," *Fuel*, **2015**, 145, 214-220
  13. Sitnov S., Feoktistov D., Kayukova G., Pronin N., and et al., "Catalytic Intensification of In-situ Conversion of High-viscosity Oil in Thermal Steam Extraction Methods," *International Journal of Pharmacy and Technology*, **2016**, 8(3), 14884-14892
  14. Vakhin A., Onishchenko Y., Chemodanov A., Sitdikova L., and et al., "Thermal Transformation of Bitumoid of Domanik Formations of Tatarstan," *Khozyaystvo-Oil Industry*, **2016**, 10, 32-34