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FEATURES OF DISTRIBUTION OF THE PARAMAGNETIC CENTERS ON THE AREA OF THE EMBA REGION OIL DEPOSITS

Abstract. In the oils of the studied deposits, we detected EPR signals both from vanadium ions and free radicals (FR). To determine their concentration, the most intense hyperfine structure (HFS) line was used among the complexes of tetravalent vanadium and a single line from the FR.

There are no noticeable changes in the density of oil and the content of vanadium (IV) in the studied wells from the area of the Jurassic deposits of the Kyrykmyltyk field. It means that on the area, vanadium content in oil does not change, there is a good hydrodynamic communication between production wells, and the Kyrykmyltyk field belongs to low-vanadium oils.

Uniform distribution of vanadium, is also established on the area of the Aptian, Albian and Cenomanian horizons of the Kara-Arna deposit and it characterizes the conditioned content of vanadium. Between the producing wells of each horizon there is observed a good hydrodynamic connection.

Keywords: complex of tetravalent vanadium, free radical, electronic paramagnetic resonance, hydrodynamic communication, conditioned content.

During the work [1], we found that in the Kalamkas field in the context of productive layers there is a clear distinction between two independent deposits by paramagnetic features and vanadium distribution (in the upper – 200g/t, in the lower -140g/t). This gave rise to the authors argue that the vanadium content is a reliable correlation feature that can be used in monitoring the development of oil reservoirs [2].

The study of the relationship between the content of stable free radicals and vanadium (IV) in oils with their physical and chemical characteristics in the area of deposits was carried out at the fields of the Emba region.

The interdependence between the content of vanadium (IV), FR and physico-chemical characteristics of the oils were studied on the area of the oil horizon for deposits Kyrykmyltyk, Kara-Arna, Karsak and Iskene. Table 1 shows the results of the determination of vanadium (IV) in oils with different densities. Table 1 shows that the relationship between oil density and vanadium (IV) content is quite clear.

The analysis of paramagnetic features of the oils of Permo-Triassic deposits of the Iskene field showed that the oils of the southern and northern fields differ sharply in vanadium (IV) content. The industrial content of vanadium was found in the oils of the southern field (table 1). These oils are also characterized by high density and high sulfur content (S ≥1 %) in contrast to lighter and low-sulfur (S ≥0,2 %) oils of the northern field. This indicates various hypergenic changes in the oils of the southern and northern fields.

IV Albian horizon deposits of Karsak – the most significant in size, thickness and oil reserves. IV Albian horizon quality oil is divided into two types: west field - low-sulphur, resinous, paraffinic; east field - low-sulphur, low-resinous, high-paraffinic, oily. As can be seen from table 1, the average vanadium (IV) content in the oils of the IV Albian horizon of the western field is 3 times higher than in the oils of the IV Albian horizon of the eastern field. Such a difference in the area of this productive horizon oil

seems to be explained either by the losses of light oil fractions of the western field, or by their migration towards the eastern field.

Table 1 – Results of the study of correlations between density and vanadium (IV) content

Field	The number of the studied wells	Oil extraction interval, m	Horizon	Change interval	
				Density, g/cm^3	Vanadium content, g/t of oil
Kyrykmyltyk	8	911 – 943	Jurassic	0,8867 – 0,8919	2,38 – 3,38
Kara-Arna	11	1047- 1074	Aptian	0,9153	110,1
Iskene:					
south field	2	659-948	Permo-Trias	0,9294-0,9397	167,7-190,8
north field	6	704-773	Permo-Trias	0,7974-0,8144	0,7-1,3
Karsak:					
west field	2	472-782	IV albian	0,9051	9,2
east field	3	481-484	IV albian	0,8612	2,9

For the oil fields Kyrykmyltyk, the relationship between FR and vanadium (IV) content, as well as physico–chemical characteristics (table 2) also established. As can be seen from table 2, the content of sulfur, resins, asphaltenes, as well as the density and viscosity of oils increases with the content of FR and vanadium (IV). There is an inversely proportional relationship between the content of FR and vanadium (IV) in oils and the yield of gasoline fractions. From the results of the analysis of the data given in table 1, it is also seen that with the increase in the depth and age of the oil, the vanadium (IV) and FR content naturally decreases. The highest content of vanadium (28 g/t) and FR falls on the Cretaceous oil horizon(table 2). Vanadium content is much higher in the lower Cretaceous deposits than in the Jurassic deposits. A similar change is characteristic of the FR. In Cretaceous sediment oils the concentration of FR is higher than in Jurassic sediments.

Table 2 - The interdependence between the content of vanadium (IV), FR and physico-chemical characteristics of low-vanadium oil from Kyrykmyltyk field

Well number	Depth, m	Age	Vanadium content , g/t	FR·10^{-17}, spin/g	Density, g/cm^3	Content, %			Fraction output up to 300^{0}C, %
						Sulfur	Resin	Asphaltenes	
11	389...396	Cret	23,2	9,2	0,927	0,35	20,0	2,56	24,1
15	930...931	J_2	2,6	2,5	0,888	0,25	8,46	0,76	28,8
11	883...891	J_2	3,3	3,6	0,887	0,39	9,01	0,29	32,3
16	469...477	Cret	17,9	5,9	0,914	0,38	14,1	1,19	15,2

At the studied wells on the area of Jurassic deposits of the field Kyrykmyltyk, there are no noticeable changes in density of oil and the content of vanadium (IV) (table.1).

The uniform distribution of vanadium (IV) is also established on the area of the Aptian horizon of the Kara-Arna field with the help of oil samples obtained from 11 producing wells (wells 23, 25, 53, 57, 66, 68, 82, 86, 87, 90, 94) (table 1). For illustration, figure 1 shows the central parts of EPR spectra of oil samples of the Aptian horizon of the Kara-Arna field (wells 82, 57, 90, 53), taken at -196^0 C, containing one of the components of the hyperfine vanadium (IV) structure and the singlet from FR.

Table 3 – Change of paramagnetic properties of Kara-Arna oil field

The number of the studied wells	Oil extraction interval, m	Age	The average content of vanadium, g/t	FR·10^{-17}, spin/g
3	510-555	Cenomanian	60,08	8,36
4	967-983	Early Albian	93,83	10,95
11	1047-1074	Aptian	102,44	11,99

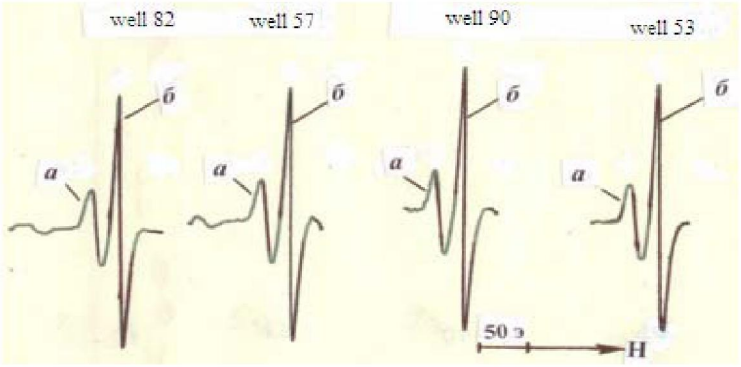

Figure 1- The Central part of EPR spectra of oils on the area of the Aptian horizon of the Kara-Arna field (wells 82, 57, 90, 53) in -196^0 C: *а* – central line of HFS from vanadium (IV); *б* – signal from FR.

As can be seen from figure 1, the intensity of both lines of the spectrum of oil samples for the studied wells is the same. This suggests that the area content of vanadium (IV) and FR in oil does not change and between producing wells, there is a good hydrodynamic connection. It should be noted that the Aptian horizon is also characterized by the conditioned content of vanadium (IV), so the industrial significance of the Kara-Arna deposit as a raw material source of vanadium is of practical interest.

Vanadium content in the oils of Emba district ranges from 60 to 126 g/t. Its increased concentration is characterized mainly by oil fields in the area, located on the South Emba uplift. Oils also belong to the category of high viscosity with a high content of resin, asphaltene and low – light fractions [3-5]. The work [6,7] discusses the patterns of distribution of vanadium in low-vanadium oils (<10g/t) from East Moldabek, North Kotyrtas, Kemerkol, South Kozha, South Tagan and Kyrykmyltyk fields, located in the South-Emba oil and gas province, united by the interdependence between the vanadium content and the physical-chemical parameters of these oils.

EXPERIMENTAL PART

EPR spectra were recorded on the E-12 spectrometer of "Varian" company. We have found EPR signals from FR and vanadium ions in the oils of the studied fields. For the determination of concentrations used the most intense line hyperfine structure (HFS) of complexes of tetravalent vanadium [5,7]. The standard concentrations were the oil from Urichtau field (from well 8) with known vanadium content (27,6 g/t) and FR (7,8·1017 spin/cm3). Samples of oil before the analysis was subjected to purification from associated water and solids by centrifugation (centrifuge T-22) when the rotation frequency of 4000 rpm. The oil samples prepared in this way were sealed in order to avoid evaporation of gasoline fractions into glass ampoules 0.2 cm in diameter and 10-15 cm in length.

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CONCLUSIONS

Evaluation of the composition and properties of oils based on the study of their paramagnetic features is proposed as a necessary step for the selection of rational ways of oil development.

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ЕМБІ МҰНАЙ КЕНІШТЕРІНДЕ ПАРАМАГНИТТІ ОРТАЛЫҚТАРДЫҢ ҚАБАТТАРЫ БОЙЫНША ТАРАЛУ ЕРЕКШЕЛІКТЕРІ

Аннотация. Біз зерттеген кен орындардағы мұнайларда ванадий ионымен бос радикалдардың ЭПР сигналдары анықталды. Концентрациясын анықтау үшін төрт валентті ванадий кешенінің және бір сызықтан тұратын бос радикалдың аса жіңішке құрылымын (АЖҚ) пайдаландық.

Қырықмылтық кенорнының юра шөгіндісінің ауданы бойынша мұнай тығыздығының және ванадидің (IV) мөлшерінің зерттелген ұңғымалар бойынша өзгерісі байқалған жоқ. Бұл дегеніміз аудан бойынша ванадий мөлшерінің өзгермейтінін , яғни зерттелген ұңғымалар арасында жақсы гидродинамикалық байланыс бар екендігін сонымен қатар Қырықмылтық кеншінің мұнай құрамы төмен ванадилі мұнайға жататынын көрсетеді.

Қара Арна мұнай кеншінің барлық зерттелген қабаттары бойынша ванадий (IV) және бос радикалдардың тұрақты болатынын және олардың жоғарғы ванадилі топқа жататынын көрсетеді..

Түйін сөздер: төрт валентті ванадий кешені, бос радикал, электронды парамагниттік резонанс, гидродинамикалық байланыс, өндірістік мөлшер.

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ОСОБЕННОСТИ РАСПРЕДЕЛЕНИЯ ПАРАМАГНИТНЫХ ЦЕНТРОВ ПО ПЛОЩАДИ В НЕФТЯХ МЕСТОРОЖДЕНИЙ ЭМБИНСКОГО РЕГИОНА

Аннотация. В нефтях изученных месторождений нами обнаружены сигналы ЭПР как от ионов вана-дия, так и от свободных радикалов (СР). Для определения их концентрации использовалась наиболее интенсивная линия сверхтонкой структуры (СТС) среди комплексов четырех валентного ванадия и одиночная линия от СР.

По площади юрских отложений месторождения Кырыкмылтык заметные изменения плотности нефти и содержания ванадия (IV) по изученным скважинам не проявляются. Это говорит о том, что по площади содержание ванадия в нефтях не изменяется, между добывающими скважинами имеется хорошая гидродинамическая связь, а само месторождение Кырыкмылтык относится к низкованадиевым нефтям.

Равномерное распределение ванадия, так же установлено по площади аптского, альбского и сеноманского горизонтов месторождения Кара-Арна и оно характеризует кондиционное содержание ванадия. Между добывающими скважинами каждого горизонта наблюдается хорошая гидродинамическая связь.

Ключевые слова: комплекс четырехвалентного ванадия, свободный радикал, электронный парамагнитный резонанс, гидродинамическая связь, кондиционное содержание.

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