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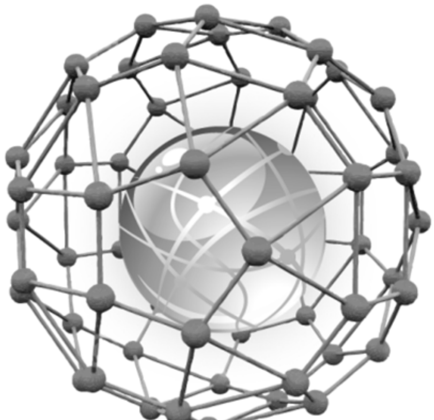

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полученные катализаторы в системе Раффа-Фентона проявляют высокую каталитическую активность по отношению к исследуемым красителям.

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THE EFFECT OF EOR TECHNOLOGIES ON THE CONTENT OF PETROPORPHYRINS AND NAPHTHENIC ACIDS OFRECOVERED HEAVY OILS FROM USINSKOYE FIELD

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The effect of EOR technologies on the contents of petroporphyrins and naphthenic acids in recovered crude oil was studied using heavy oils from Usinskoye oil field (Republic Komi), which has high viscosity and high content of resins and asphaltenes, metallporphyrins, naphthenic acids. It is found that EOR system in combination with thermal-steam treatment injection brings about an increase in the content of vanadyl porphyrins of crude oils. As a result of the EOR system injection, the naphthenic acids content would decrease in heavy oils.

Key words: heavy oil; EOR technologies; naphthenic acids; petroporphyrins

The production of heavy oils in most oil fields of Russia is carried on using water shutoff technology. The Enhanced Oil Recovery (EOR) technologies used for the development of heavy oils 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. The use of EOR 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 surfactant-based systems, chemical reagents which cause generation of carbon dioxide and ammonia, thereby creating an alkaline buffer system. When used in combination, the above EOR technologies may cause chemical transformation of crude oil due to the exposure to high temperatures. 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 heavy oil [1–4]

Heavy crude oil, is a complex mixture of organic compounds predominately composed of hydrocarbons, and often contains large amounts of other compounds such as organic and inorganic sulfur species, trace metals, metallporphyrins and naphthenic acids. Naphthenic-based crudes contain a higher percentage of naphthenic acids. Naphthenic acids constitute about 50 wt % of the total acidic compounds in crude oils [5]. Porphyrins and their geological derivatives (vanadyl and nickel porphyrins) are unambiguous indicators of biological activity because they are widely distributed among all living organisms and crude oils on planet and, unlike other molecules such as amino acids, lipids, and polyaromatic compounds, cannot be abiotically produced in measurable amounts under natural conditions [6, 7].

The effect of EOR technologies on the composition and properties of recovered heavy crude oil was studied using samples from Usinskoye oil field of the Permian-Carboniferous formation Usinskoye oil field (Republic Komi). The studied crudes has high viscosity and high content of resins and asphaltenes [8].

Three samples were collected from No. 2752 well, two samples – from No. 2805 well, two samples – from No. 3418 well and two samples – from No. 4243 well at different time intervals after the EOR system injection (treatment) in 2014 year.

The separation of heavy oils was carried on by the method of liquid-adsorption chromatography on a column packed with Al_2O_3 (4^{th} 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' (Carl Zeiss Jena, Germany), using the adsorption band intensity in the visible region of the spectrum (550 nm for nickel porphyrin and 570 nm for vanadyl porphyrin) [9, 10].

Using alcohol solution of potassium hydroxide, potentiometric titration was carried on to determine the carboxylic (COOH) group and content of naphthenic acids in crude oil samples [11].

The results of variation in the contents of petroporphyrins and naphthenic acids are listed in Table.

As is seen from the data presented in Table heavy oils contain substantial amounts of vanadyl (133 – 288 nmole /g) and nickel (44 – 71 nmole /g) porphyrins. The vanadyl porphyrins content has increased in the crude oil samples collected from No. 2752, 2805, 3418 and 4243 wells two months after the EOR system injection. Evidently, the vanadyl porphyrin content of crude oil is turning back to the initial value with time. It can be seen that the nickel porphyrin content remains practically unaffected by the EOR system injection.

The effect of EOR system treatment on the content of petroporphyrins and naphthenic acids in heavy oils from Usinskoye oilfield

Well No.	Date of sampling	EOR technologies	Petroporphyrin content, nmole /g		Content, wt %	
			nickel	vanadyl	COOH – groups	naphthenic acids
2752	07.2014	–	56	223	0,33	2,1
	09.2014	after treatment	46	288	0,15	1,0
	10.2014	after treatment	44	238	0,09	0,6
2805	07.2014	–	41	171	0,29	1,8
	09.2014	after treatment	47	220	0,11	0,7
3418	08.2014	–	69	263	0,11	0,7
	10.2014	after treatment	71	277	0,10	0,6
4243	07.2014	–	44	133	0,14	0,9
	10.2014	after treatment	66	205	0,13	0,8

As can be seen from the data presented in Table naphthenic acid content in the heavy oil from Usinskoye oilfield is in the range from 0,6 to 2,1 wt %. The content of acids would first (2–3 months) to decrease (2752, 2805, 3418 and 4243 wells) as a result of treatment to finally return to the initial value. Consequently, it is more economical to isolate these acids from naphthenic-based crudes.

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

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ПРИМЕНЕНИЕ ПРОТОЧНЫХ СПОСОБОВ ПРОБОПОДГОТОВКИ ДЛЯ ХИМИКО-АНАЛИТИЧЕСКОГО КОНТРОЛЯ ЗАГРЯЗНЕНИЯ ПОЧВ

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Химико-аналитический контроль окружающей среды необходим для получения объективных данных о содержании загрязняющих веществ, в том числе токсичных. Нефтепродукты входят в число часто определяемых компонентов в объектах окружающей среды. При мониторинге состояния почв для определения нефтепродуктов используют в основном ИК-спектрометрический и флуориметрический методы анализа. Стандартные методики анализа почв на содержание нефтепродуктов указанными методами отличаются довольно длительной пробоподготовкой, включающей извлечение нефтепродуктов из образца (экстракция) с помощью органического растворителя, выпаривание и реэкстракцию (при флуориметрическом