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SURFACTANT–POLYMER FLOODING: GEOCHEMICAL MONITORING OF THE PROPERTIES OF FORMATION FLUIDS AT THE IMPACT AREA

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ABSTRACT

Chemical flooding methods improve oil extraction after standard waterflooding processes. Chemical EOR methods modify different properties of fluids and/or rock to mobilize the remaining oil. It is expected that the residual oil will be different in properties than conventional. A new technology is presented to study a surfactant–polymer flooding, based on a periodic sampling and measuring properties of oil and water during 15 months. The study area is a terrigenous reservoir with 3 chemical injection wells and 16 production wells. High-precision mass spectrometry methods were carried out on each sample, which made it possible to evaluate the effectiveness of ongoing work on chemical flooding. At each sampling date, 2D reservoir model was built to track these changes in the study area. It is shown that the composition of the water has changed - highly permeable channels were closed and formation waters were involved in the production. The properties of oil have also changed - depending on the site of impact, there are areas with more degraded oil in production after injection of chemicals. Geochemical monitoring shows the redistribution of filtration flow directions in the reservoir volume.

Keywords: surfactant-polymer flooding, geochemistry, terrigenous reservoir, field development, remaining oil.

INTRODUCTION

Waterflooding currently stands as the primary field development method, involving the injection of water into the oil reservoir through injection wells. As water moves through the formation, it displaces hydrocarbons from the rock towards production wells, optimizing asset development efficiency. The main reason for using surfactants is to lower the interfacial tension (IFT) between water and oil. Surfactant-polymer flooding, considered a tertiary oil production method, aims to artificially alter the physical and chemical properties of oil [8,9]. Surfactants improved separation of hydrocarbon particles from the rock, while polymers increase water viscosity, facilitating a more even displacement of oil from the reservoir to production wells.

Thus, polymer flooding is a dual technology employed to enhance oil recovery. It achieves this by increasing the sweep factor of the formation through displacement and concurrently reducing residual oil saturation in the washed zone. This reduction is achieved by minimizing the ratio of the mobility of oil to that of the displacing agent within the formation [1].

Chemicals that increase oil production an industrial scale are constantly growing in development and use [2,8]. Generally, the surfactants application refers to the effective methods of chemical oil recovery [6,7,11,12]. The difference in low oil-water interfacial tension and ultra-low surfactant tension makes a decisive factor in oil displacement efficiency [10,11]. Conformance control consists in injecting slowly cross-linking compositions into the bottomhole zone of the formation, which penetrate deep into the formation for considerable distances and redistribute filtration flows in the formations, especially in case of usage low mineralized water [5,6,7]. The source of water and oil entering wells is determined using geochemical methods [3].

There are 2 theories about changing the chemical composition:

Firstly, polymer flooding consists in mixing long chain polymer molecules with the injected water in order to increase the water viscosity. This method improves the vertical and areal sweep efficiency because of improving the water/oil mobility ratio. Therefore, we receive a different composition of water during chemical flooding - previously non-drained zones begin to work. Secondly, the oil that remains inside the reservoir - immobile oil - has a different composition than mobile oil. In this work, we tested both theories (Figure 1).

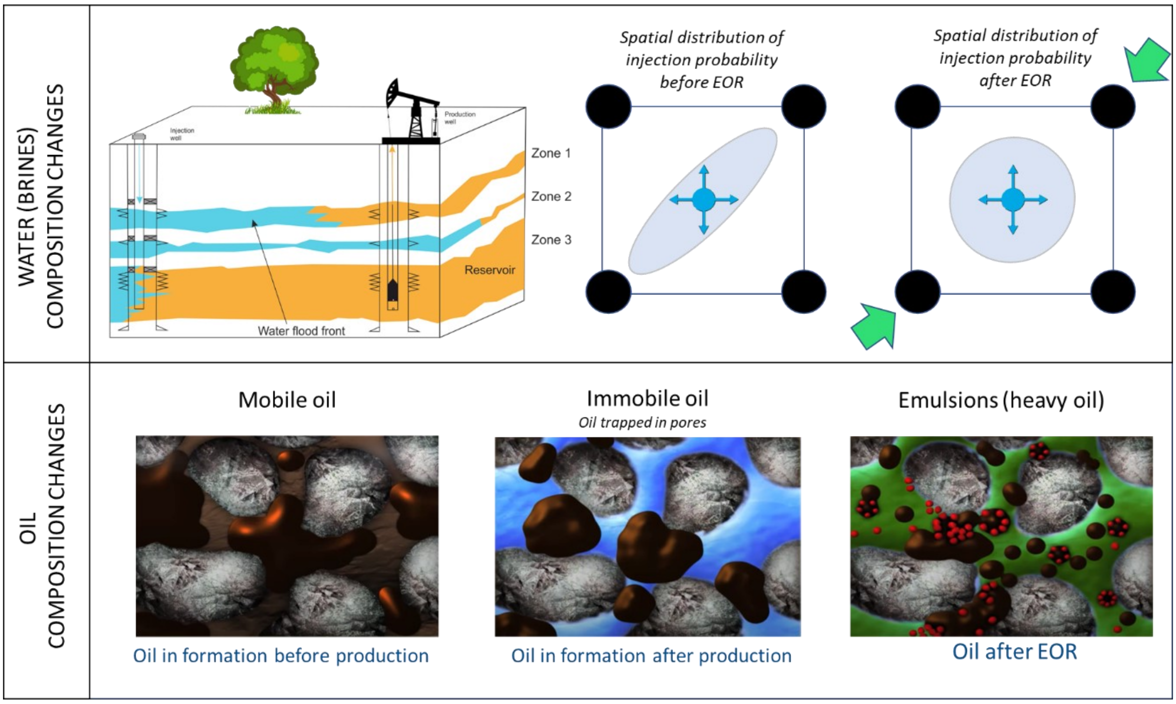


Figure 1. Theoretical approach

MATERIALS AND METHODS

The object of the study is production wells with perforation for the Lower Carboniferous System, namely the Bobrikovian horizon, and the Tournaisian stage. **The Tournaisian Stage (C_1t)** overlies the Famennian sediments. Deposits of the stage are widespread and are composed of gray or dark gray bituminous clayey limestones with interlayers of dolomites, mudstones, and clays.

The Bobrikovian (C_1bb) horizon is represented by brown, fine-grained, quartz, oil-saturated sandstones with interlayers of black, thin-layered, calcareous, micaceous mudstones and highly clayey, dark gray, fine-grained siltstones. The thickness of the horizon is small, ranging from 4-11 m.

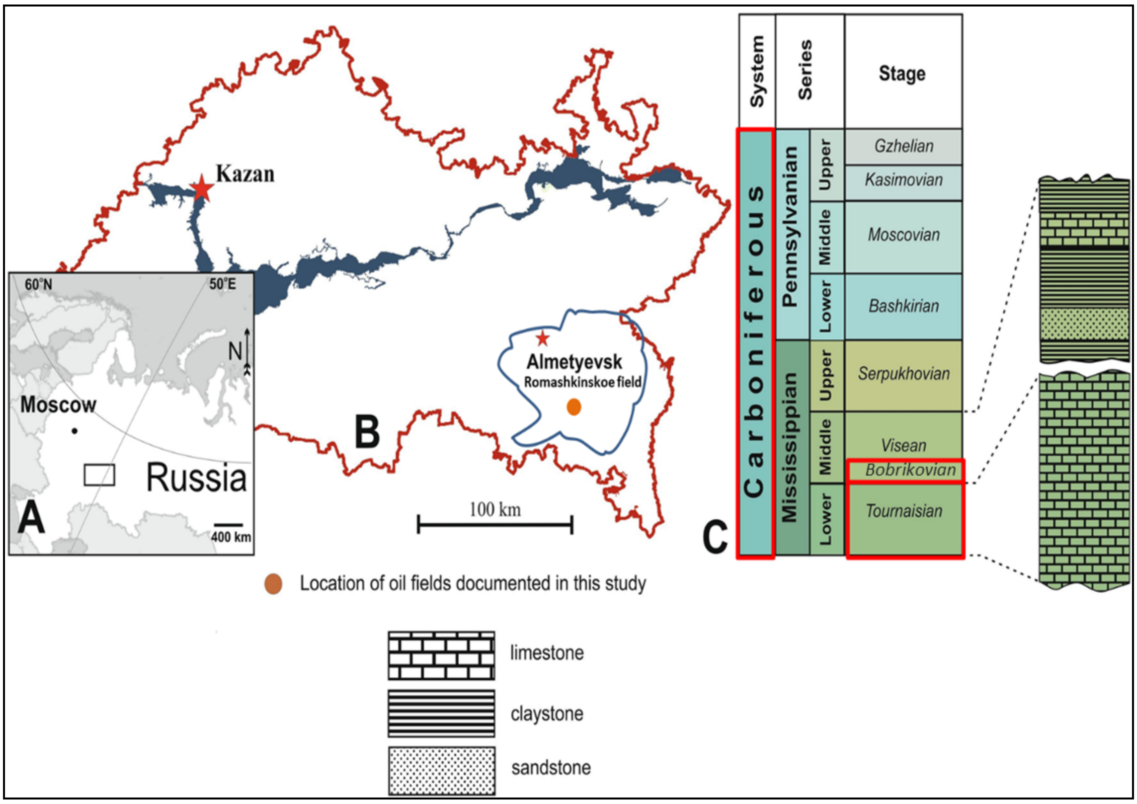


Figure 2. Overview map. Stratigraphic scale of the region under study

Lower Carboniferous deposits in the studied field began to be developed in the late 1970s [4]. Throughout the entire period, intensive fluid production was carried out, technologies were used to maintain reservoir pressure by pumping water into 5 injection wells. This led to the formation of washed channels. To close them, chemicals were injected into injection wells No 1, 2 and 7 (Figure 3).

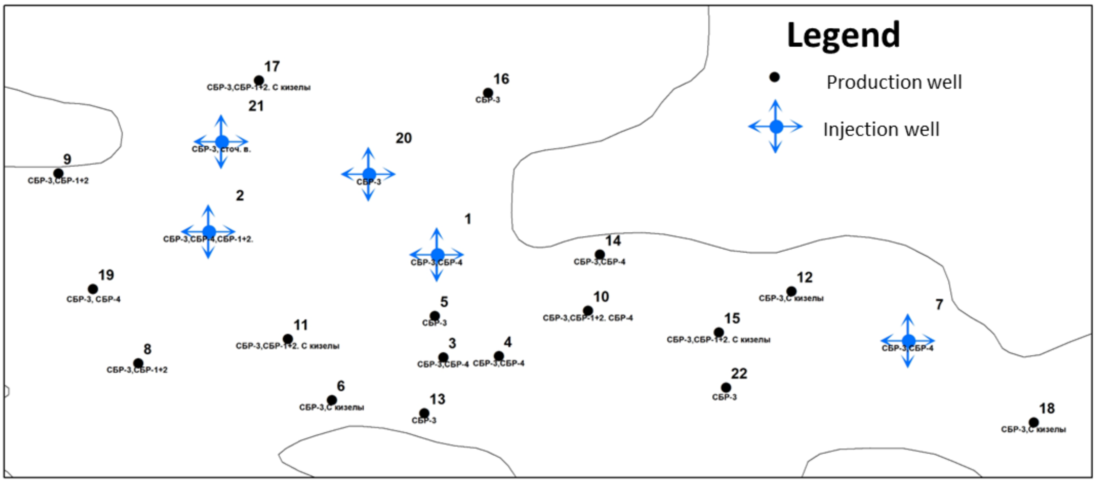


Figure 3. Map of the location of wells in the study area

Reservoir fluid was collected according to the established schedule. Background sampling was carried out prior to injection of chemicals to characterize the area. Samples were then collected on the same date each month and delivered to the laboratory. Sample preparation was carried out: separation of the aqueous phase from the hydrocarbon phase by centrifugation and thermal standing, filtration of water from hydrocarbons and mechanical impurities. The composition of water and oil was studied from all production wells. Laboratory data included analysis of oil by GC-MS and water by TXRF. The result obtained was compared with the well production data (Figure 4).

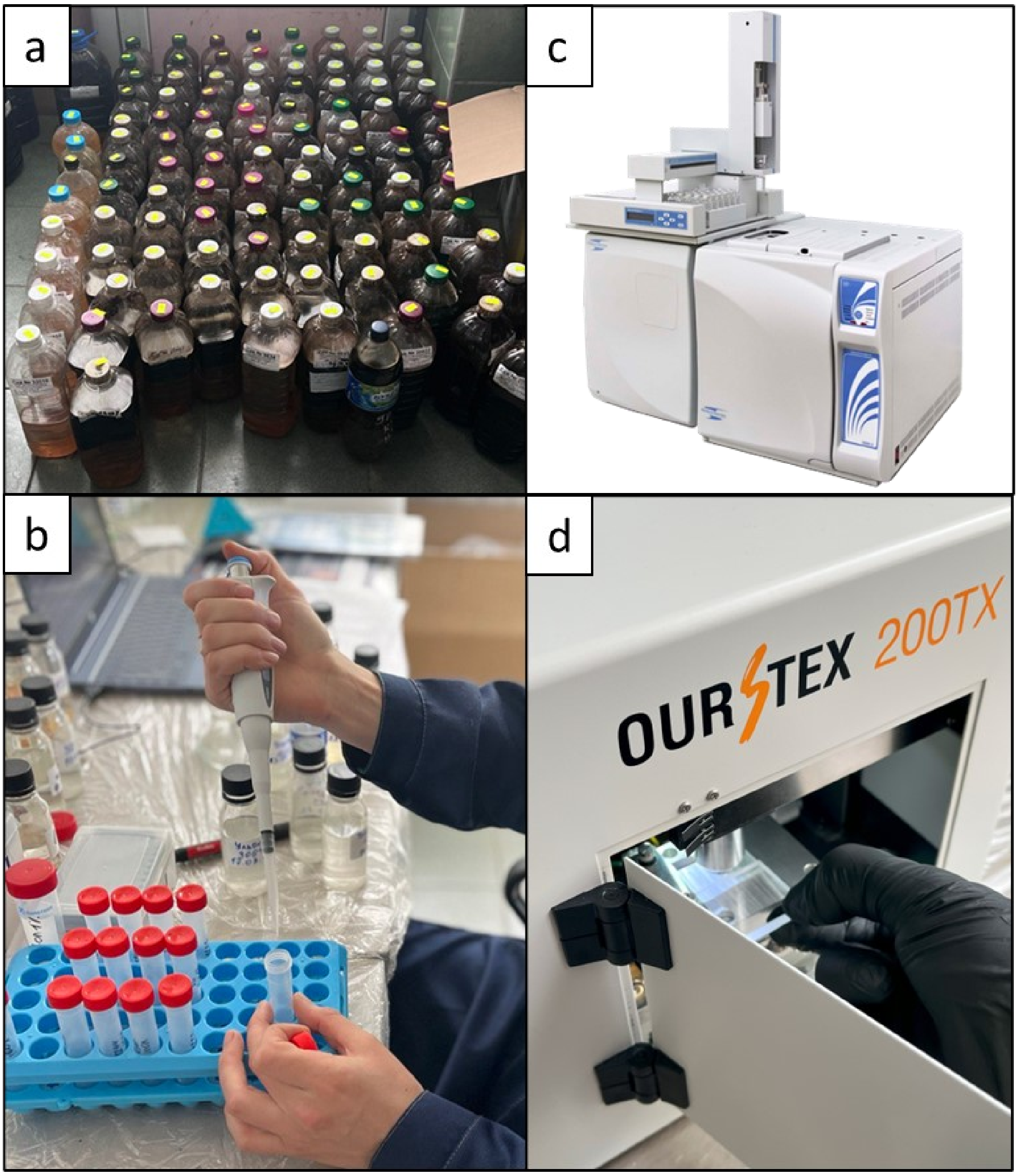


Figure 4. Photo collection of the laboratory work. (a) Oil and water samples, (b) Water preparation processes, (c) Thermo ISQ GC/MS Mass Spectrometry Facility, (d) Total reflection-type X-ray fluorescence Spectrometer, TXRF

The Gas chromatography–mass spectrometry (GC-MS) method is a combination of two powerful analytical tools: gas chromatography, which provides highly efficient separation of complex mixture components in the gas phase, and mass spectrometry, which allows identifying both known and unknown mixture components [15]. It is intensively used in **organic petroleum geochemistry**. Extracts from geological samples represent complex mixtures of organic compounds, some of which are biomarkers that provide information about the origin of oil and sedimentary conditions. Biomarkers are hydrocarbons with preserved carbon skeleton of ancient organisms located at great depth and underwent physical and chemical transformations [16].

Geochemical studies of formation water are carried out by measuring the elemental composition of produced reservoir water and water from waterflooding system using high-precision mass spectrometry methods at wells **(TXRF).**

Wells selection to determine the characteristic features of the reservoirs is carried out by an automated algorithm. At the selected wells the patterns of produced fluid composition changes are established both by area and by section. The obtained data are processed by methods of mathematical statistics (Maximum likelihood estimation method for linear normal model), which allow to determine the origin of watercut source during well operation in several strata with joint production [13, 14].

RESULTS

Water composition. For the purpose of geochemical monitoring, 153 samples of wellhead samples were studied in the field under study for 15 months, including reference wells to the **Bobrikovian horizon**, water samples from injection wells. The results of geochemical measurements of water are shown in the Table 1. M12 is a geochemical parameter that reflects the ratio of trace elements. It is a characteristic of the hydrogeological environment, it is stable - therefore it is selected for geochemical monitoring.

Table 1. Distribution of the concentration of the hydrogeochemical marker M12

Type	Well No	Wellhead Sampling Data							
		03.12.2021	**02.02.2022**	**19.03.2022**	**03.05.2022**	**17.06.2022**	**05.09.2022**	**24.11.2022**	**12.02.2023**
Production wells	**5**	61,2	72,4	61,5	113,9	39,6	56,2	39,3	20,4
	13	133,2	186,9	147,6	204	223,4	199,7	309,8	232,6
	3	63,1	65,4	122,9	100,5	37,3	39,4	48,2	42,3
	22					98,7	106,8		77,1
	14	52,4	96,1	168,6	55,1	70,5	50,5	74,5	64,6
	19		133,7	156,8	222,8	298,1	240,7	249,8	289,4
	4	57,1	42	43,2		42,3	39,2	33	
	18	144	140,1	154,4	155,5	258,1	279,1	240	280,8
	12	49,2	68,5	40,1	51,5	70,8	8,3	39,9	36
	6	91,1	64,1	77,4	75,2	58,5	95,7	57,2	73,4
	16	143,5	123,6	47,9	106,7	105	92,7	82,5	98
	17	99,7	113,5	150,7	102,51	116,9	113,8	160	88,6
	15	34,7	75,6	27	49,1	34	17,1	20,2	29,1
	11	94,5	77,9	52,2	90,4	158,9	111,3	113,4	76,1
	9	72,6	72,5	65,4	147,6	131,8	141,7	124,3	129,2
	8	71,1	67,7	48,1	207,7	107	101,2	55,4	60,7
	10	41,5	50,6	43,6	47,1	33,1	30,4	31,9	46
Injection wells	**2**	10,1	10,1	10,1			2,2		
	1	10,1	10,1	10,1			2,2		
	7	10,1	10,1	10,1			2,2		

As of the date of background sampling, before the injection of chemicals - December 3, 2021, the composition of the injection water contains **10.1 M12**, and the most typical production well No. 18 **M12 is 144,0.** It can be noticed how this parameter changes during geochemical monitoring, for each wellhead sampling data.

Also, according to these data maps of the studied composition of samples for each date of sampling were built (Figure 5). The greatest changes are recorded in the 3rd sampling data, 5 months after injection of the surfactant-polymer composition. During the monitoring period (2022 – 2023 years), these differences increased. The red color - an increase in the M12 marker - is typical for the marginal zones - it means that previously non-drained zones began to work and high permeability channels from injection wells closed.

Examining the performance of wells throughout the entire monitoring period (refer to Figure 6) leads to the following conclusions:

• For example, production **well No. 18** is located at the edge of the reservoir. The geochemistry of injected and produced waters is different, which means there is no water breakthrough from **injection well No. 7**. In the last year, there has been an increase in oil flow rates and a decrease in water cut. The water produced by the well is reservoir water; there is a smooth increase in the M12 index from 144 to 281. Previously undrained source reservoir water is involved.

• For production **well No. 5**, a change in the hydrogeochemical situation is noted, namely a decrease in the share of water from injection **(K_{inj})** in the period from May 2022 to February 2023. Change in M12 from 61 to 114. This is due to a decrease in the volume of injection through injection **well No. 1** and injection of chemicals. However, then there is an increase in K_{inj}, a decrease in M12 towards the injected water, which on the last date of sampling became equal to 20. Thus, the ending of the work of chemicals in the formation water was recorded. The calculated water fraction from the injection well at the last sampling date is 0.88.

• **Production well No. 9** is located near the injection **well No. 2,** in the marginal zone. According to it, a change in the hydrogeochemical situation towards formation water is observed - a change in M12 from 73 to 148 over time, the M12 reading remains high, and the influence of injected water on the water cut of the well is reduced. As of the last sampling date, **K_{inj}** was close to 0, the effect of chemical injection is still going on.

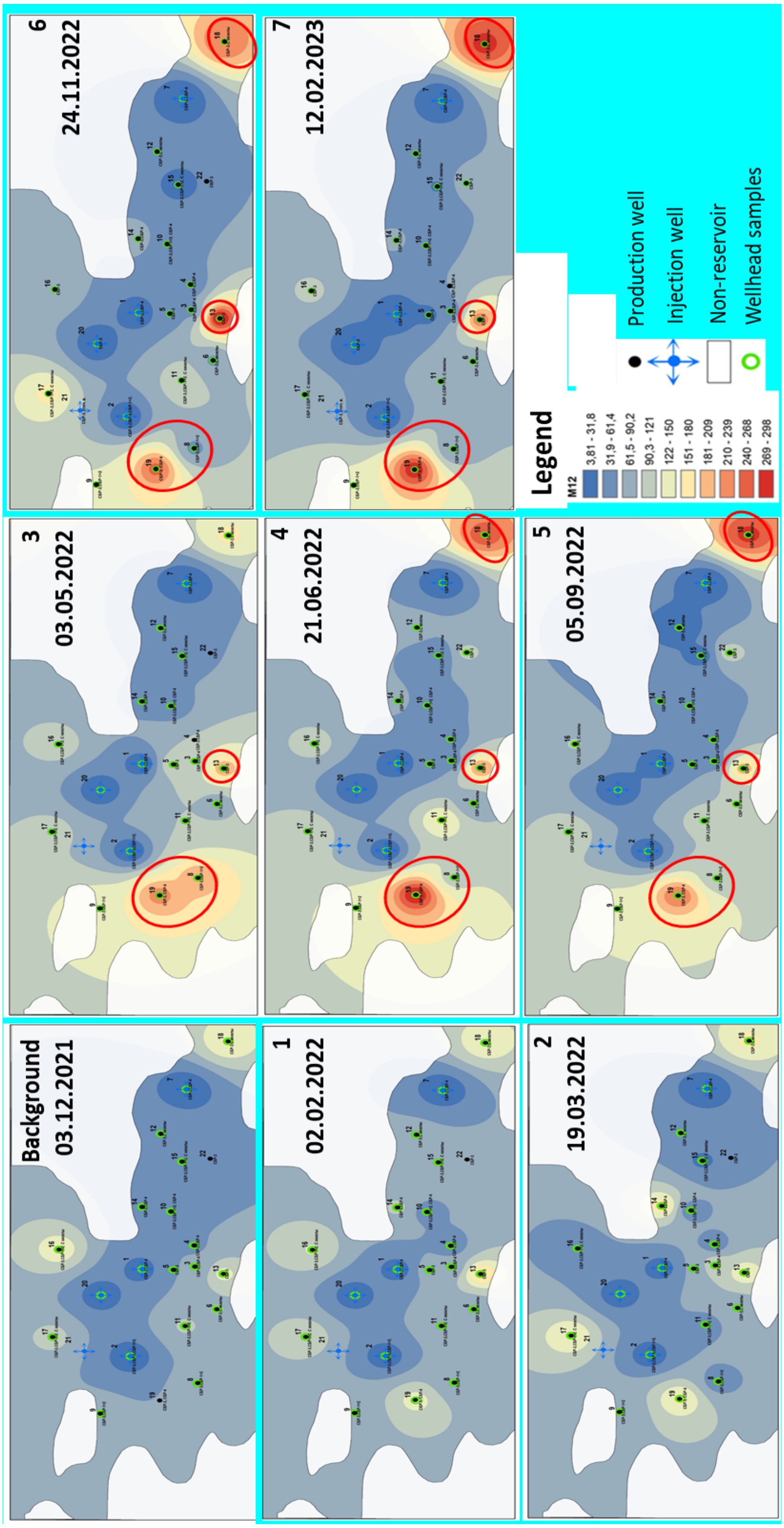
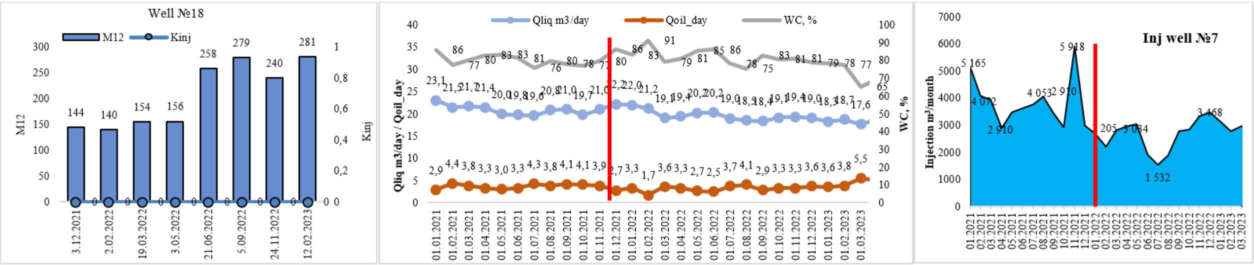
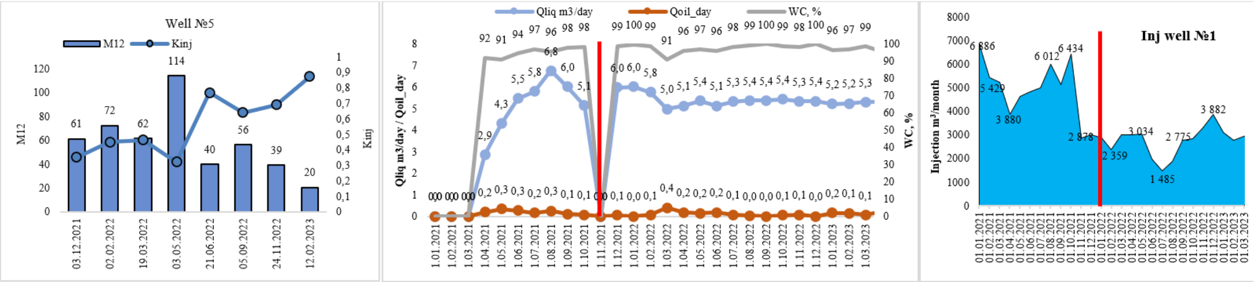


Figure 5. Distribution map of hydrogeochemical marker M12 concentration

Well №18



Well №5



Well №9

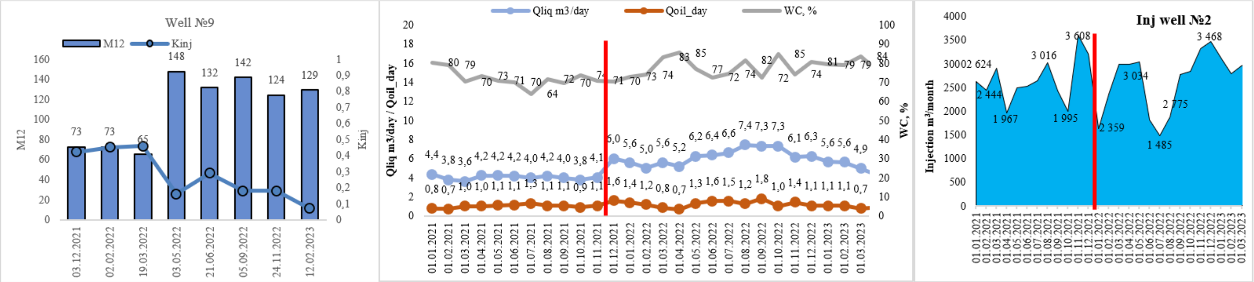


Figure 6. Development parameters

Oil composition. The hydrocarbon phase study by GC-MS method used classical biomarkers, of which the isoprenoid coefficient **Ki** is the most indicative. The coefficient of isoprenoidity characterizes the change of concentration of the main isoprenoid alkanes pristane (Pr) and phytane (Ph), evaporating in the region of boiling temperatures of alkanes of composition n-C17 and n-C18, and indicates the features of the oil types formation. Value Ki ≥ 1 clearly indicates the course of oil biodegradation processes. Chemically, the informativeness of this indicator is based on the known regularities in the rates of decomposition of alkanes of normal and isoprenoid structure, leading to a decrease in the numerical values of the indicated ratio with an increase in the transformation degree.

The most degraded oil by biomarker Ki is observed in well No. 18, and during monitoring this parameter increased from 0.84 to 1.09-1.13, which indicates the additional recovery of biodegraded (immobile) oil (Figure 7). On the map, in the zone of high values, the area includes the following wells: No. 15, 8 and 12. In most other wells, the Ki parameter ranges from 0.84-0.86 to 0.93.

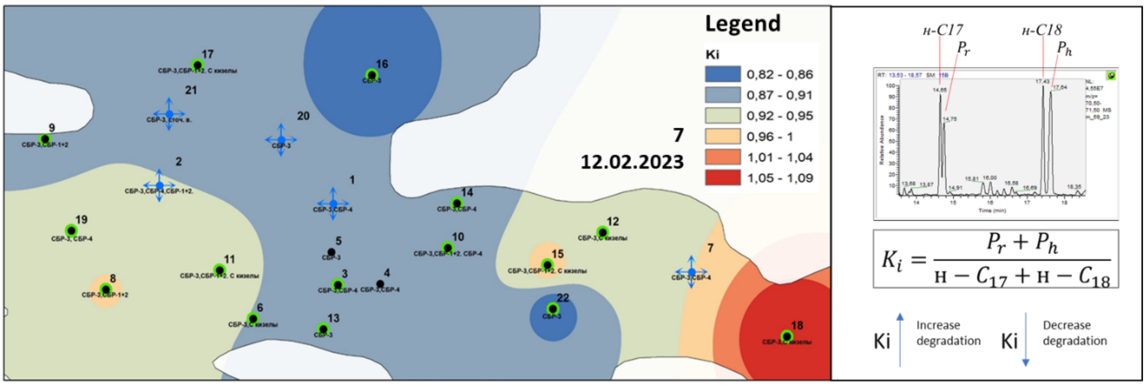


Figure 7. Map of the distribution of Ki (oil composition, 12 February 2023)

Rapid growth of the isoprenoid coefficient indicates additional recovery of more degraded oil not previously involved in production, which allows us to assess the effectiveness of the oil recovery increase method (wells No 18 and 13).

The Figure 8 of combination of GC-MS data (for hydrocarbon phase) and TXRF data (for water phase) shows a correlation confirming the inflow of another oil and another water - formation water, richer in M12 marker content, not affected by injection system.

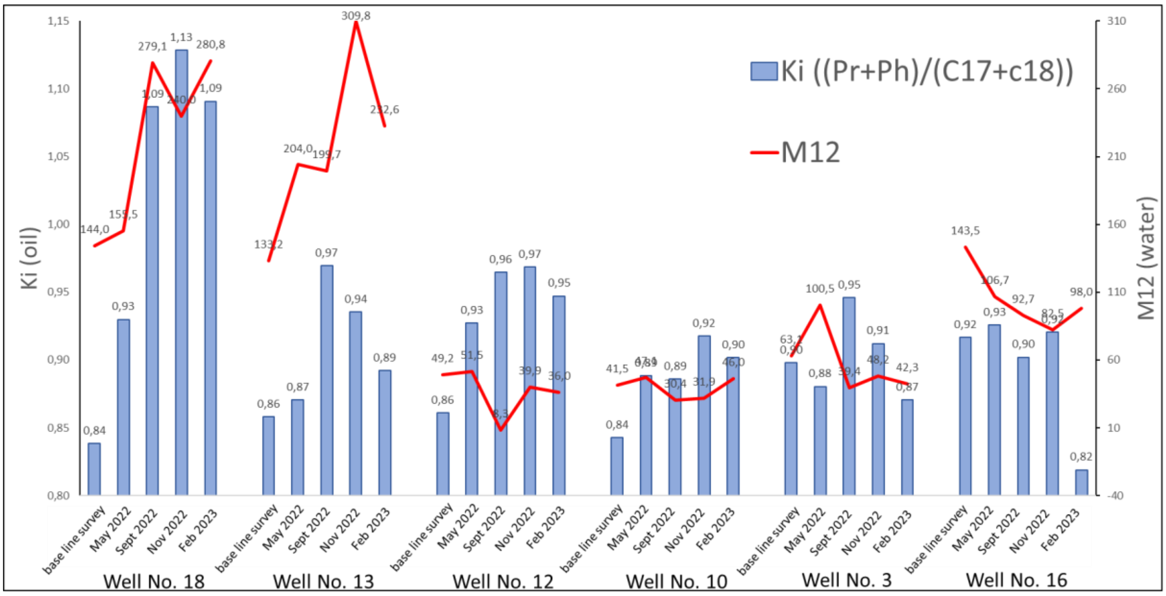


Figure 8. Combining the results of the composition of water (brines) and oil

CONCLUSION

Based on the results of geochemical monitoring, there is a change in filtration flows in the reservoir, a change in the geochemistry of producing wells, and the “switching on” of other previously non-drained zones in the development area. An increase in the content of the M12 marker shows the closure of highly permeable channels and the involvement of formation water in the production, which is different from the injected one. According to the results of the calculation algorithm for the influence of the waterflooding three groups of wells were identified:

I Group of wells without changes: No. 13, 18, 19.

II Group of wells with the dynamics of increasing changes: No. 15, 12, 4, 14, 3, 16, 8, 11, 22, 5, 6.

III Group of wells with the dynamics of decrease changes: No. 9, 10, 17.

Based on the results of the geochemistry of the hydrocarbon phase, the coefficient Ki was selected, which made it possible to determine the degree of degradation of the studied samples during the monitoring process. The most degraded oil according to the Ki biomarker is observed in well No. 18, and during monitoring this parameter increased from 0.82 to 1.09–1.13, which indicates additional recovery. The change in Ki in oils correlates with the change in M12 in formation water - in the case of the involvement of previously non-drained zones, other water is involved - and another oil - more degraded, not mobile before.

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