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Production Logging Using Quantum Dots Tracers®

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Abstract

Conventional production logging tools proved to be efficient in vertical wells. When it comes to work in horizontal laterals production logging becomes much more complex. Common challenges are layered flow of reservoir fluid, deviation, wellbore accessibility, and stagnant zones along lateral. The tracer technology features a synthesis of a combination of marker-reporters made of a few quantum dots and a mixture of the polymer-based chemical composition. Quantum dots are nanocrystals produced using the process called colloidal synthesis. A single quantum dot is compounded of few hundred atoms and as small as 2-10 nanometer in diameter. Colloidal quantum dots irradiated with a laser emit light of different colors due to quantum confinement. The emittance of a particular specter of light can be detected using flow cytometry method. Several quantum dots joined together creates a unique and traceable marker-reporters element. There could be many unique tracer signatures (over 60). Utilization of quantum dots exclude any chance of misinterpretation while identifying tracers in samples of formation fluid. To achive superior accuracy in tracer identification we use software based on "machine learning". Qualitative and quantitative analysis of quantum dot marker-reporters in samples of formation fluid allows making informed conclusions about the performance of productive intervals of a horizontal well. Application of the technology showed the following benefits: the possibility of monitoring inflows for a long time, in contrast to a one-time logging operation; a significantly lower resource intensity and cost; confidence in conditions when the traditional downhole logging operations are complicated. Quantum dot tracer technology allows solving a number of problems, such as: post-fracturing inflow profile evaluation extended in time; assessment of each production interval in regard to water and oil production; optimization of technical solutions for well completions in the early stages of field development, such as number of ports; analysis of hydrocarbons extraction ratio; detailed information in the analysis of mutual influence of neighbouring wells in the oilfield. The application of the technology is particularly effective in the early diagnosis of water breakthrough, which allows enough time to choose the right technology for water shut off operation. Ultimately, this fact reflects in declining production rates and increasing incurred costs Major benefit is an ability to monitor production per zone at any time during five (5) years after deploying tracer-containing material downhole. Implementation of the technology is time efficient and does not require field equipment as well as crew for operation, which reflects on operating costs carried by customers.

Introduction

One of the newest technologies to emerge, providing information on native oil and water flow from each hydraulically stimulated stage of unconventional wells, involves the use of hydrocarbon-soluble chemical tracer tagging. The key to this technology is the use of specialist tracers that are manufactured in the form of emulsions. These are added to marked propant to be pumped at each fracture stage. The tracer is applied with the proppant and transported deep into the fracture matrix. The selected specialized tracers are hydrophobic but have a very strong affinity for either hydrocarbon liquid or water. Wherever the marked propant contacts hydrocarbon in the fractures, the tracer will move across from the aqueous phase into the in-situ hydrocarbon.

In recent years, there has been a singnificant interest in tracer research in the world, but very few materials have been published on the tests that confirm or deny the claimed advantages of these technologies.

Often, oil and gas production companies make decisions to use tracer technologies without any testing, based only on the reputation of the supplier company, the duration of its presence in the market or value.

The reason for this may be the lack of unified test methods, as well as the experience of sharing best practices between subsoil companies. At the same time, tracer technologies are a relatively new field of activity in the field of well research, therefore, it is necessary to approach the assesment of technologies on the basis of objective indicators.

Classification of tracer technologies for the study of wells

Tracer (marker) methods of research use the following marking technologies:

- Chemical water and oil-soluble reagents (fluorescent, ionic and organic tracers);
- Quantum markers-reporters;
- Chemical DNA tracers.

Fluorescent and ionic tracers as indicators for the study of oil-and-gas bearing reservoir have been widely spread since the last century. Despite the fact that these reagents are of relatively low cost, their weakness is the difficulty in reliable quantifying the well flow log during monitoring, as well as limiting possible combinations of tracers to no more than 5-7 units.

Quantum markers-reporters are polymeric monodisperse microspheres. Their identification is carried out by the method of flow cytometry with the use of algorithms of machine learning [1, 2, 3].

Chemical DNA tracers are long polymeric molecules consisting of repeating blocks - nucleotides. Identification of these tracers is carried out by liquid chromatography in combination with mass spectrometry [4].

A general comparison of tracer technologies is presented in Table 1.

Table 1—parison of tracer technologies for the study of wells

№	Parameter	Chemical water and oil-soluble reagents				Chemical DNA tracers	Quantum markers-reporters
		Fluorescent tracers	Ionic tracer	Organic tracers			
1.	State	Dry powder/liquid				Polymer	Polymer matrix
2.	Type	5-7 (sodium fluorescein, disodium salt of eosin, erythrosine, rhodamine)	5-7 (ammonium rhodanate, sodium, carbamide, urea, sodium nitrate, ammonium; thiourea)	3-4 alcohols (isopropanol, butanol), isomers fluorobenzoic acid		No data	60 and above
3.	Water/oil solubility	Very soluble in water	Very soluble in water	Soluble in both oil and water		Soluble in both oil and water	Soluble in both oil and water
4.	Resistance in reservoir conditions	Mean	Mean	High		High	High
5.	Marker identification method	Fluorescence microscopy	Photometry, electron-paramagnetic resonance spectroscopy	Chromatography		Liquid chromatography, mass spectrometry	Flow cytometry
6.	Analyzer	Fluorate, fluorescence microscope	Fluorate, photoelectric colorimeter	Chromatograph		Chromatograph, mass spectrograph	Analytical hardware and software complex
7.	Sensitivity	From 1 mg/t	No data	From 1 mg/t		No data	No restrictions
8.	Additional restrictions	1. Absence of mono-dispersion. 2. "Slushed" by polar organics. 3. Presence of similar substances in the reservoir	Difficulties in quantitative determination due to low accuracy.	1. High duration of research. 2. Difficulties in application for industrial scales.		-	-

In addition to the type of tracers used, it is possible to classify tracer technologies by the following criteria:

1. By the type of wells:
   – Vertical;

– Horizontal;
– Diviated;
– Multilateral.

2. By the method of introducing tracers into the well (reservoir):
   – Application of packaging arrangements (downhole casings, filters of special constructions, cassettes);
   – Application of a marked polymer-coated proppant under a multifrac;
   – Injection of tracers with liquid (HFT-fluid, acid solutions).
3. By the method of lab analysis:
   – Manual (for example, using microscopes);
   – Automated (with the use of modern software and hardware systems and self-teaching software).

Features of the application of quantum markers-reporters

Tracer technology is based on the use of markers-reporters from quantum dots embedded in the polymer coating of a proppant used to fasten cracks during a multi-stage hydrofrac (Figure 1) or their use in packaging arrangements of completion (Figure 2).

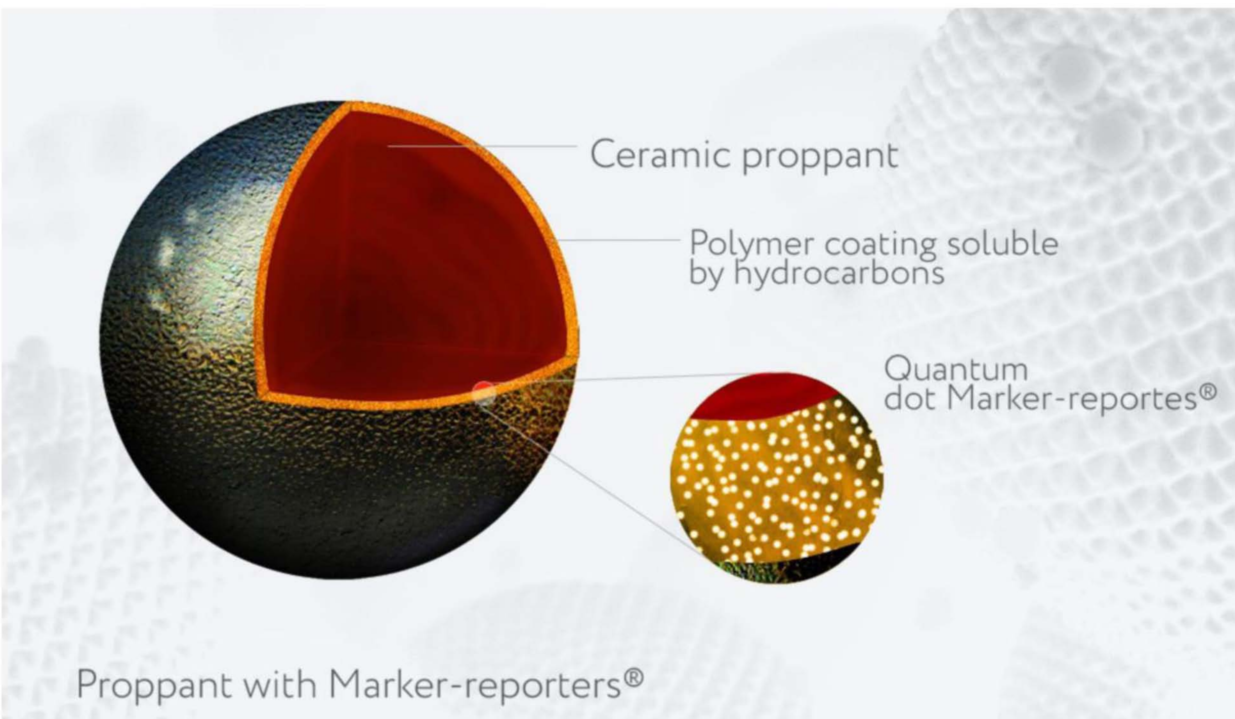

Figure 1—Marked polymer-coated proppant

Figure 2—Cassette for marking a horizontal section with marked granulate

In the process of operation, the markers-reporters are washed out by the flow of reservoir fluid for a long period of time. When collcting samples from the wellhead and subsequent laboratory tests, the analytical hardware-software complex tracer determines the concentration of markers for each code (Figure 3), that allows us to estimate the quantitative distribution of oil and water phases for each horizontal section.

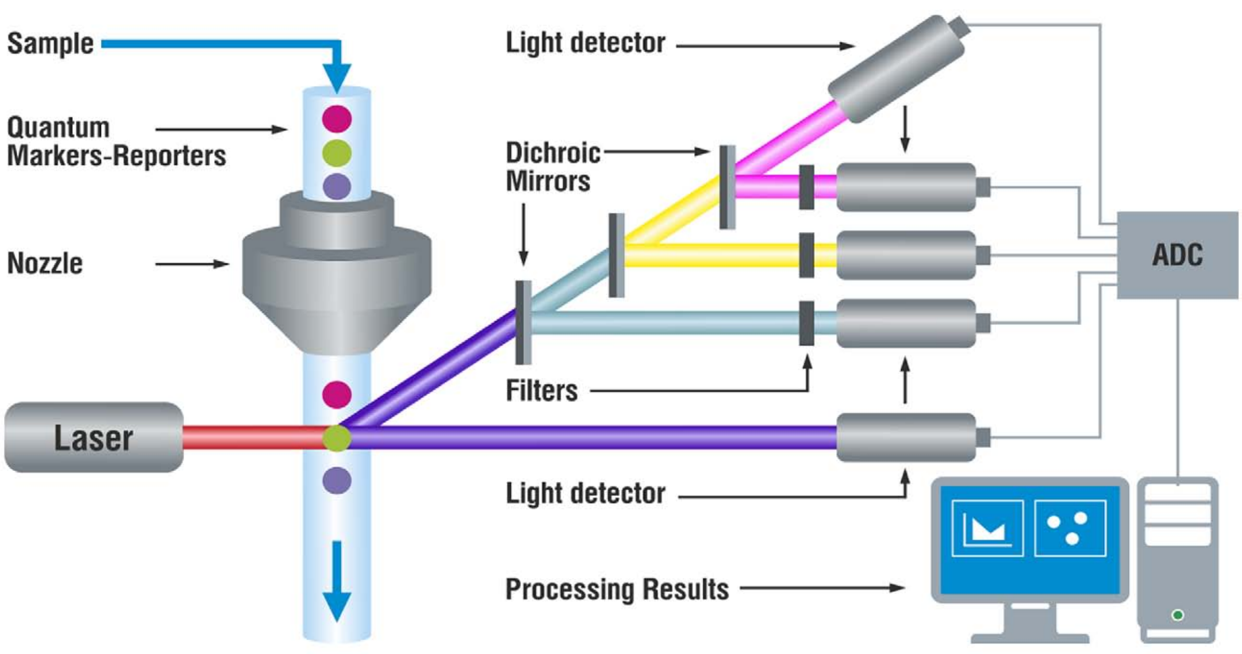

Figure 3—Analytical hardware-software complex, impementing the identification of markers- reporters by a flow cytometry method

The main advantages of using quantum markers-reporters include:

1. Monodispersity of markers by size.
   The lack of monodispersity of tracers introduces considerable margin of error for reliable quantitative analysis, since particles of different sizes have different sedimentation rates and, as a consequence, different relative flow velocities in the wellbore. Particles of small sizes will be removed by the fluid flow faster than in case with larger particles. In addition, particles of different sizes differ in their ability to move with the reservoir fluid in the reservoir.
2. Automated identification of markers in samples of reservoir fluid.
   Identification of markers is carried out with the automated software and hardware complex in the mode of piece-by-piece analysis without the use of microscopes. When analyzing samples, a strict number of markers-reporters is identified in as pieces per each sample, that ensures high accuracy of the studies and eliminates errors related to the human factor.
3. Uniform output of markers for an extended period of time.
   Markers-reporters, sewed into the polymer matrix of the proppant or promo powder, ensure the stability of the concentration of their release from the polymer coating.
4. A large number of signatures (codes) of markers.
   At present, it is possible to synthesize more than 60 unique signatures of markers for hydrophilic and hydrophobic polymer coatings that allows to carry out the diagnosis and monitoring of 30 horizontal sections simultaneously
5. No restrictions for the use of markers in reservoir conditions.
   show high physical-and-chemical stability, as well as resistance to the influence of aggressive media and reservoir thermobaric conditions.

Internal Testing

Work experience with different customers in different regions has shown that additional tests are needed to confirm the operation of the technology and the claimed advantages.

To this end, conducted a wide range of laboratory tests of various marker systems, including:

1. basic tests for the physical-and-chemical stability of markers and the polymer matrix (temperature stability, stability of the concentration of markers' separation, acid resistance, resistance to hydrogen sulfide);
2. tests for determining the basic permeability (conductivity) of a proppant pack;
3. crash test on study of the effect of propane destruction on the intensity of markers' separation;
4. marked proppant compatibility tests for HFT-gel.

Basic tests on the physical-and-chemical stability of markers and the polymer matrix

Tests on temperature stability and stability of the concentration of the markers' separation in time. The tests were carried out on a column filled up with proppant through which the target fluid (water, oil) was passed at various temperatures and with a fixed flow rate (Figure 4), after which fluid samples were collected and analyzed in the laboratory.

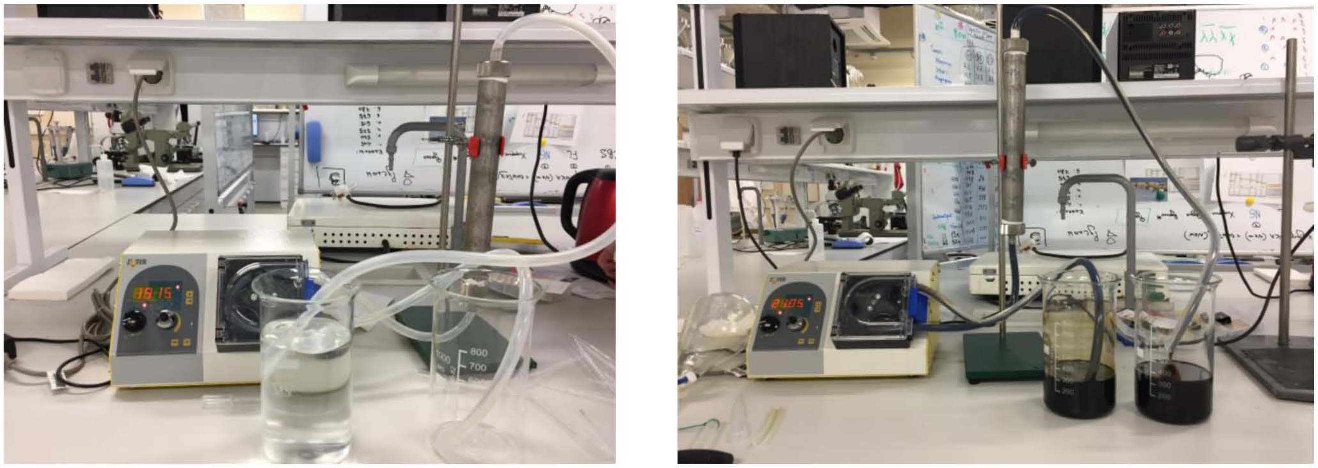

Figure 4—Laboratory facilities for testing with water (left) and oil (right)

Figures 5-6 show the results of tests on the stability of the concentration of markers' separation in time at different temperatures and a with a fixed flow rate for the hydrophilic (HP) and oleophilic (OP) marked proppant.

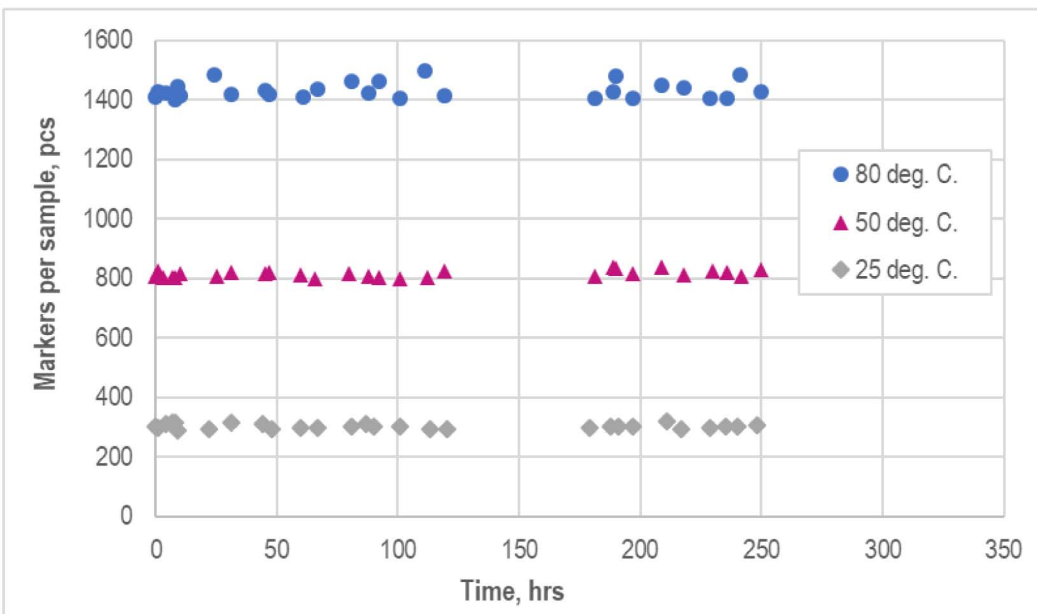

Figure 5—Dependence of the number of markers released from the hydrophilic proppant (HF), on the time at different temperatures and a fixed flow rate

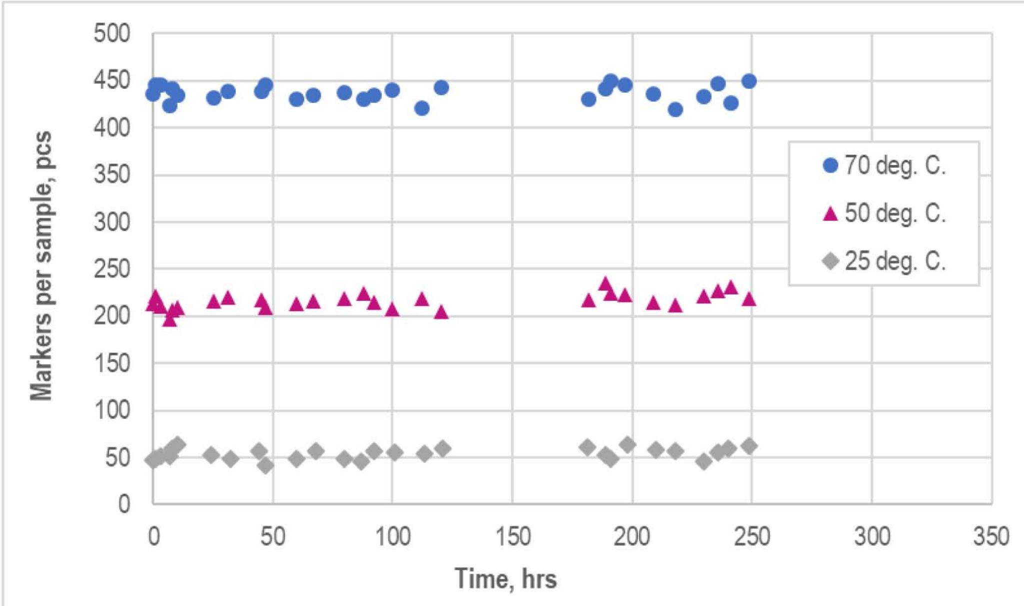

Figure 6—Dependence of the number of markers separated from the oleophilic proppant (OF), on the time at different temperatures and a fixed flow rate

As the result of tests, there has been a stable concentration of markers' separation from the polymer coating of the proppant at different temperatures.

Tests for reserching the dependence of the markers' separation in the water-oil medium at different values of water encroachment. The tests were carried out in a similar manner on a column filled out with proppant through which the water-oil mixture was passed at different values of water encroachment, after which fluid samples were collected and analyzed in the laboratory.

Figures 7-8 reflect the results of a study of the dependencies of the markers' separation in the water/oil phase on the fluid flow rate at different values of water encroachment.

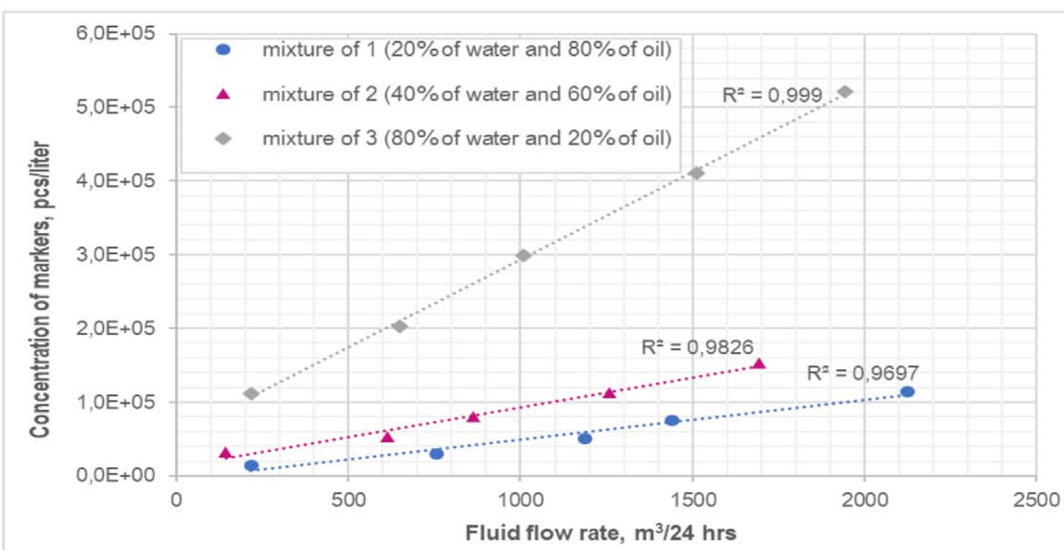

Figure 7—Dependence of the number of markers separated from a mixture of proppants in the water phase, on the fluid flow rate at different values of water encroachment: mixture of 1-20% of water and 80% of oil; mixture of 2-40% of water and 60% of oil; mixture of 3-80% of water and 20% of oil

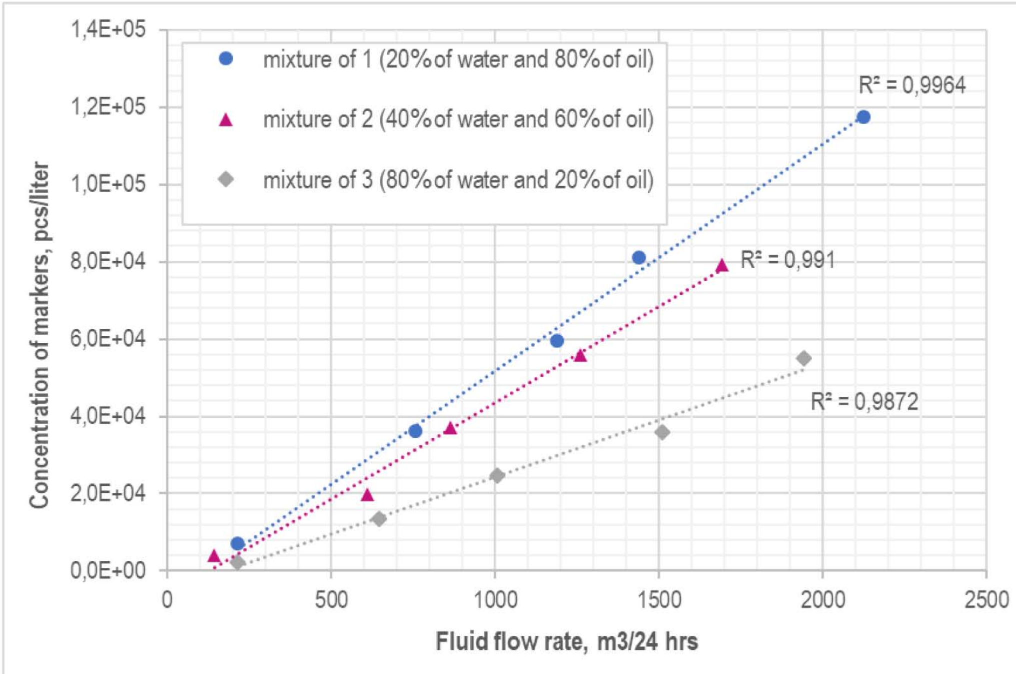

Figure 8—Dependence of the number of markers separated from the proppant mixture in the oil phase, on the fluid flow rate at different values of water encroachment: mixture of 1-20% of water and 80% of oil; mixture of 2-40% of water and 60% of oil; mixture of 3 - 80% of water and 20% of oil

The experiments have proved that the character of the separation of markers from the polymer coating, depending on the fluid flow rate, including the water-oil mixture at different values of water encroachment, is linear, which makes it possible to unambiguously quantify the distribution of the horizontal wellbore inflow profiles.

Tests on acid resistance. The tests were carried out by gravimetric determination of the change in the mass of the sample of hydrophilic (HF) and oleophilic (OF) proppants after treatment with working solutions of acids:

- mixture of concentrated hydrochloric and hydrofluoric acids;
- hydrochloric acid solution.

The results of the acid resistance tests are shown in Table 2.

Table 2—Test results on acid resistance

№	Type of acid	Relative change in mass of the marked proppant after treatment, %	The requirement of the quality standard (GOST R 51761)	Compliance with the quality standard
1	A solution of a mixture of hydrochloric and hydrofluoric acids with a mass ratio of 4:1	7,0	8,0	Yes
2	Hydrochloric acid with a concentration of 15%	0,9	1,0	Yes

According to the test results, it was found that the marked proppant shows a low solubility in acids and meets the requirements of quality standards.

Tests on hydrogen sulfide resistance

The tests were carried out by saturating water and oil with hydrogen sulphide by bubbling through them the gas obtained from the reaction of iron sulphide (II) with hydrochloric acid and passing the target fluid saturated with hydrogen sulfide through a proppant column to determine the mass loss of the proppant.

The results of testing for resistance to hydrogen sulphide have showed that the weight loss is:

- 0.07%, in a solution of H_2S-saturated water;
- 0.04%, in a solution of H_2S-saturated oil.

A low loss of mass indicates the inertness of the polymer coating in relation to hydrogen sulphide.

Figures 9-10 show the dependence of the number of markers separated from the proppant on the time of fluid passage at a fixed flow rate of 200 m^3/day

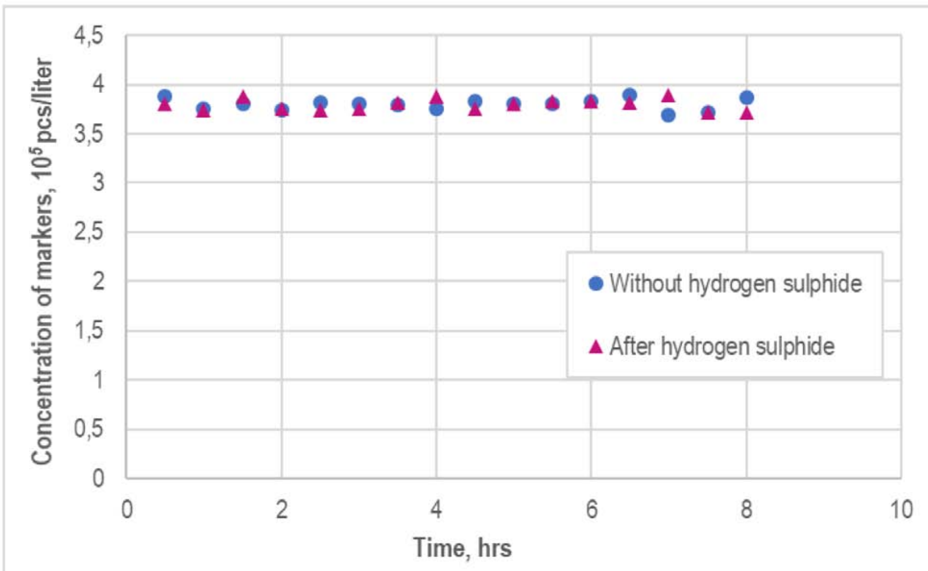

Figure 9—Dependence of the concentration of markers in a water sample on the time of passage through a marked proppant of H_2S-saturated fluid

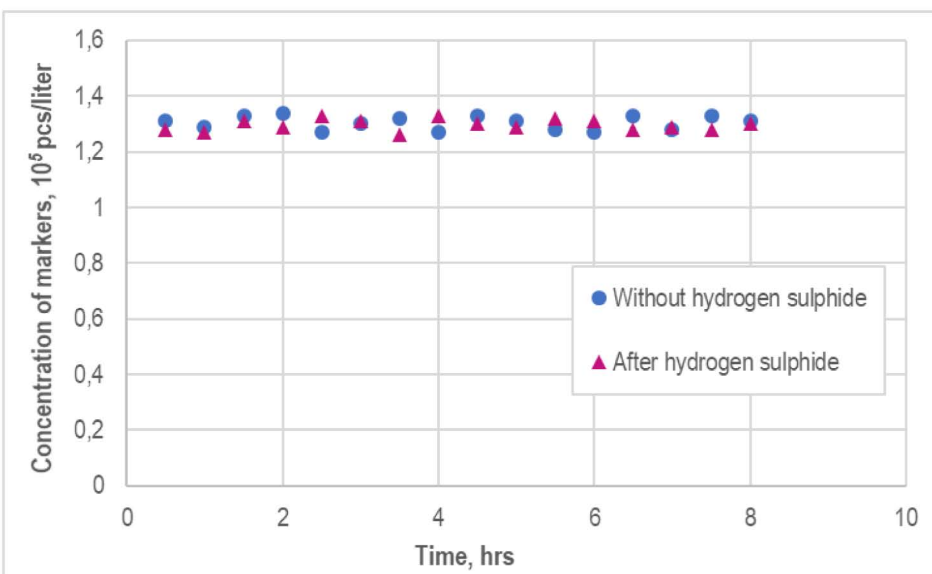

Figure 10—Dependence of the concentration of markers in the oil sample on the time of passage through the marked propane of H_2S-saturated fluid

The experiments have shown that the polymer coating of the marked proppant is chemically resistant to hydrogen sulfide. The presence of hydrogen sulphide in the reservoir fluid also does not affect the separation of markers from the polymer coating of the proppant.

Tests on determination of the basic permeability (conductivity) of a proppant pack

This experiment was based on the technique for measuring the long-term specific conductivity according to ISO 13503-5. The tests were carried out with marked proppant (fraction 30/50 GS) and conventional uncoated proppant (fraction 30/50 UP) in order to compare the permeability and conductivity of both proppants in the following conditions:

- temperature of 100 °C;
- geostatic pressure of 300, 450, 550 and 700 atm.

Dependences of the permeability and conductivity of proppant packs on the geostatic pressure are shown in Figures 11-12.

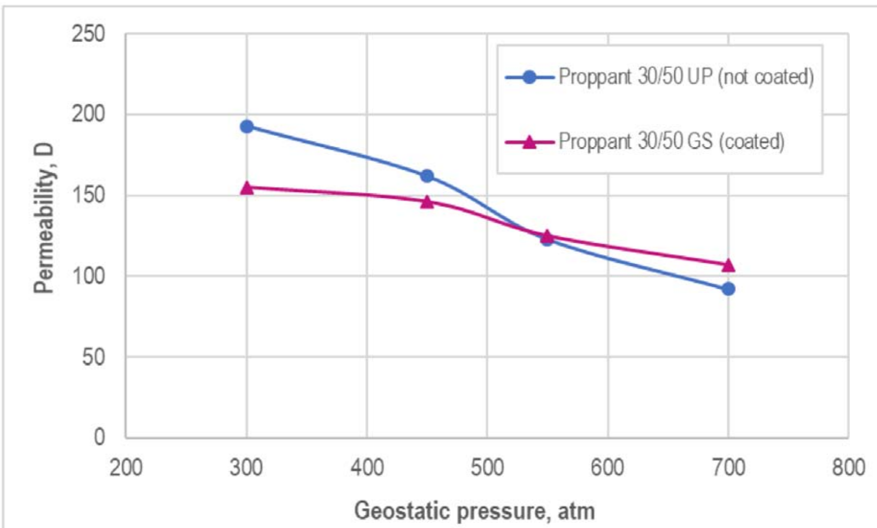

Figure 11—Dependence of permeability of proppant packs on the geostatic pressure

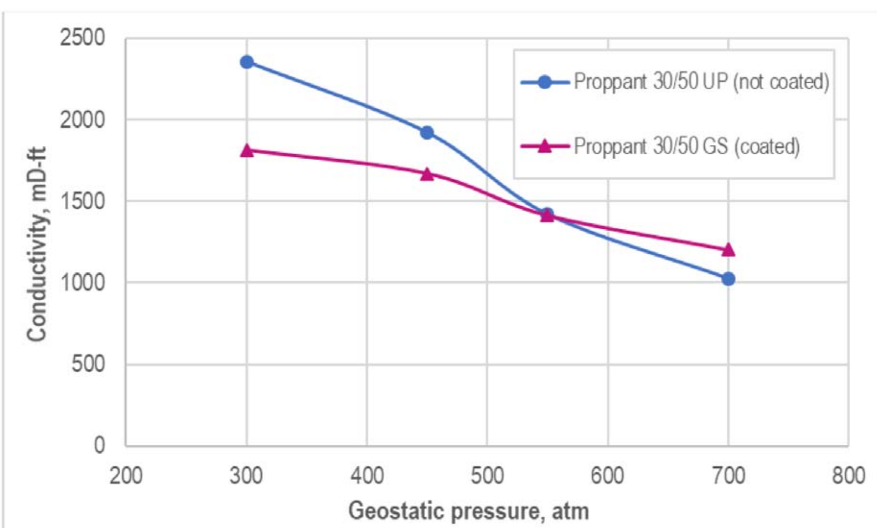

Figure 12—Dependence of the conductivity of proppant packs on the geostatic pressure

The results show that with geostatic pressures of less than 550 atm, the permeability and conductivity of the proppant pack for the marked proppant of 30/50GS is lower than that of the uncoated 30/50 UP proppant that is a typical property of polymer-coated proppants.

However, at a geostatic pressure of 550 atm and above, the conductivity of the proppant pack of the marked proppant becomes higher. This is most likely due to the fact that in the polymer-coated proppant, the contact area increases as compared with the conventional one. The presence of a polymer film on the proppant at high pressure and temperature leads to the adhesion of individual grains to each other, therefore, its destruction occurs in a smaller amount. Thus, the fragments of the uncoated proppant are more likely to plug the inter-porous space and reduce conductivity.

It should also be noted that the permeability reduction of the polymer-coated marked proppant has made up 31%, and of the uncoated proppant 52%, which is an additional argument for the use of polymer- coated proppants.

Crash test on study of the effect of proppant destruction on the intensity of separation of markers

The crash test was carried out by means of a marked proppant grinding with a mechanical agitator at a rotation speed of 2400 rpm. Then, the samples of mixtures of the destroyed and undestroyed proppant were prepares; the mass fractions of the destroyed proppant were 0, 5, 10, 15 and 20%. Each sample was filled up with a distilled water with the same mass as the weight of the sample.

The results of the experiment are shown in Figure 13.

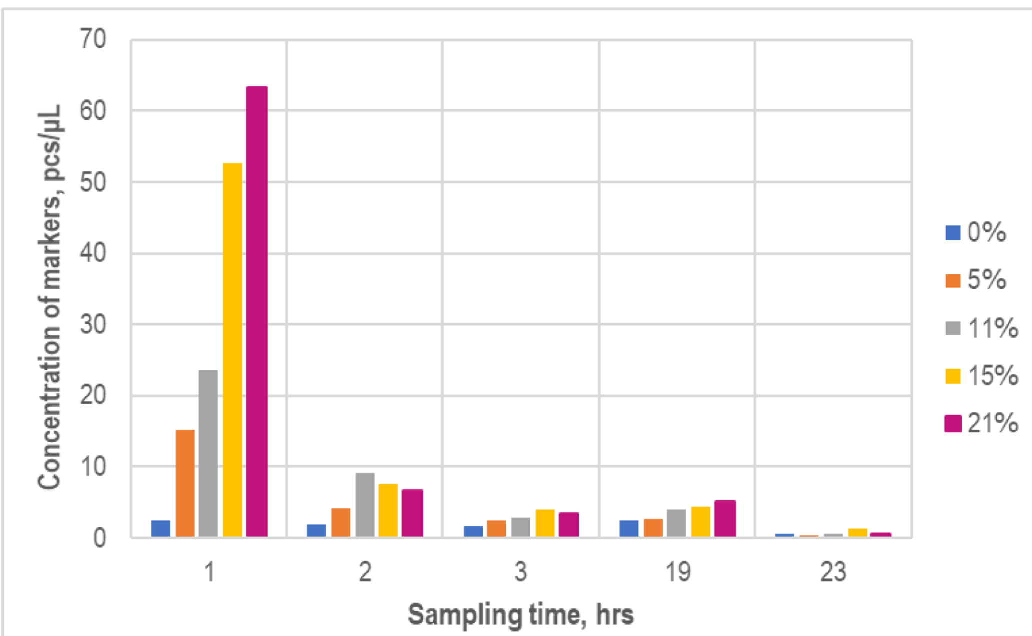

Figure 13—Dependence of concentration of markers on the time at various mass contents of the destroyed proponant

The experiment has showed that physical destruction of the marked proponant leads to a rapid washout of the markers from the destroyed grains, as a result of which there is a short-term jump in the content of markers in the samples. At the same time, the described effect quickly disappears due to the removal of a significant part of the markers by the fluid. Thus, partial destruction of the proppant in reservoir conditions can be registered in one of the single samples but does not significantly affect the content of markers in long-term studies.

Tests on the compatability of the marked proppant with HFT-gel

The purpose of the tests was to determine the effect of the polymer coating of the marked proppant on the stability and profile of the fracturing HFT-gel using oxidative destructors at a temperature of 110 °C.

During the tests, the proppant was added directly to the linear gel and mixed for 5 minutes. Then pH-parameter was measured and afterwards the gel was crosslinked with proppant, and again the pH- parameter was measured. Further, the crosslinked gel was filtered out of this mixture to determine its rheological properties.

The results of the tests are shown in Figure 14.

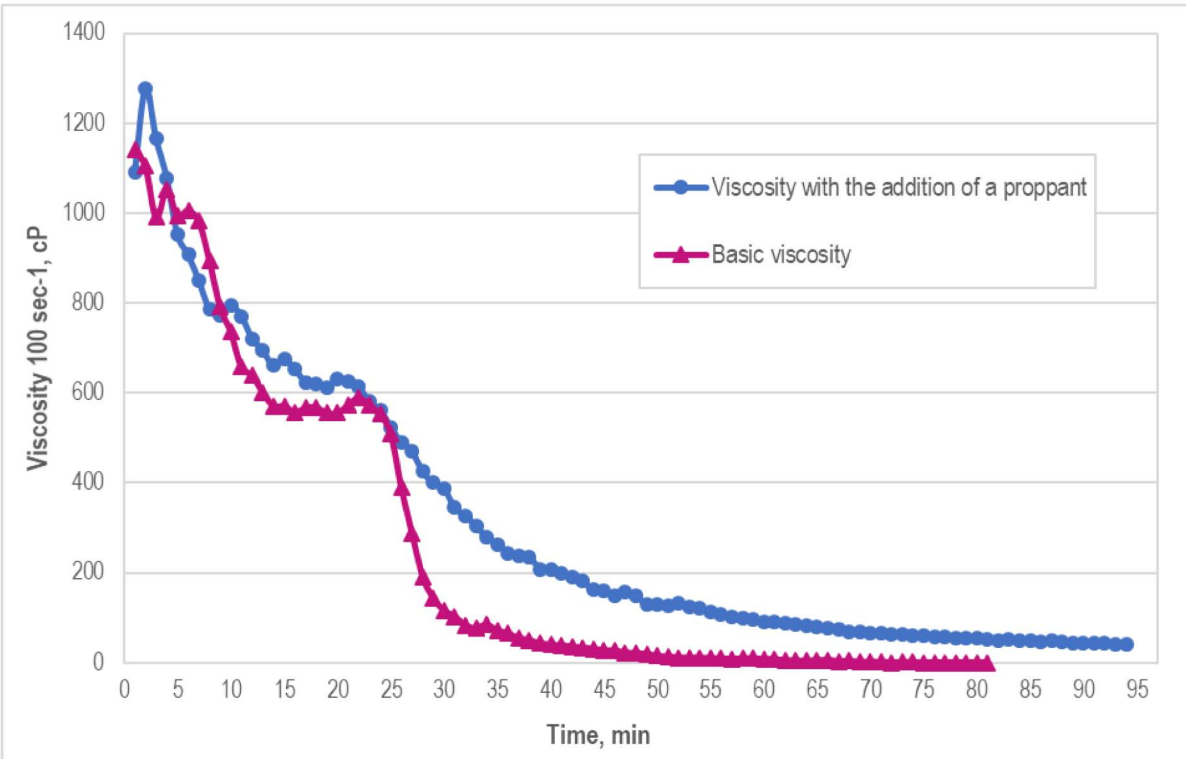

Figure 14—Results of tests on the compatability of the marked proppant with a water-based HFT- gel with the addition of a capsized destructor

According to the results obtained, the addition of a marked proppant to a water-based HFT-fluid does not lead to its physical, chemical and rheological changes, but it slightly reduces the activity of the oxidative destructor, which should be taken into account when designing a HFT-design.

External Independent Tests and Effectiveness of a tracer technology

Conventional production logs are used to determine dynamic and static wellbore flow parameters. These logs are used for multiphase flow identification in the wellbore and sometimes, behind casing or tubing. The most common application of production logging is the measurement of a well's production profile, and the distribution of flow into or out of the wellbore. Conventional production logging that requires lengthy and pricy coiled tubing or wireline intervention operations however is still frequently and commonly used by main O&G production complanies.

Despite all advantages that this technique has there're still many drawbacks that most of times doesn't represent proper reservoir production data. That leads most of operators to make uneccessarry following conclusions that could cause unfortunate operational and financial risks by having additional well operations or even risks accompanied with decreasing oil recoivery from particular stimulated well or whole oil reservoir. Therefore, nowadays all operators are looking for optimizing economical costs and increasing effectiveness of receiving downhole information.

One of solutions explained in this article is a multiphase production monitoring. Therefore, finding tools defining an efficiency and accuracy of such tracer multiphase monitoring technique could be one of the main chellenge for hydrocarbon production companies.

Meawhile one of the most effective proving instruments remaind is laboratory test. Running and testing tracer technology in the lab could provide precise and most accurate result whitout having wrong interpretations or human error even

The key parameter for conducting external tests with the participation of customers and independent experts is the verification of the technology for the accuracy of the quantitative determination of markers.

Tests on the accuracy of the quantification of markers were conducted with the involvement of two customer companies (for the proppant solution and for the powder) independently of each other. The tests were carried out according to the following procedure:

1. The manufacturer of markers-reporters (hereinafter referred to as the contractor) has provided for the independent commission of the customer a marked proppant/marked powder of 5 different signatures (codes).
2. The Commission, in the absence of GeoSplit LLC, has prepared several mixtures containing different combinations of signatures, at the same time the samples of each signature were weighed on a laboratory scale; the measured mass was known only to commission members. Each sample of the mixture was signed with a conventional cipher.
3. Samples of the mixtures were transferred to the research laboratory of GeoSplit LLC. In the presence of the commission, water containers (2% KCl solution) of 1 liter each were prepared, after which the mixture samples were placed in appropriate containers.
4. Next, each container was mixed by a mechanical agitator, after which a laboratory analysis of liquid samples taken from the containers was carried out.

The results of the comparison of the data determined by the contractor and the commission's actual data for the marked proppant are presented in Table 3, for the polymer granulate to mark the equiplment for completing the wells - in Table 4.

Table 3—Results of quantitative determination of markers by a proppant

Lab Test results				Actual data on the commission of the customer					Discrepancy
Mixture	Cipher	Code	%	Mixture	Cipher	Code	%	Mass, g	%
1	WT	1	24	1	WT	1	24,99	249,95	0,99
	WG	2	25		WG	2	25,34	253,35	0,34
	WR	3	16		WR	3	14,99	149,98	1,01
	WU	4	0		WU	4	0	0	-
	WP	5	35		WP	5	34,68	346,88	0,32
	Total		**100**		Total		**100,00**	1000,16	-
2	AR	6	29	2	AR	6	26,78	273,76	2,22
	AQ	7	18		AQ	7	18,16	185,62	0,16
	AT	8	11		AT	8	12,37	126,47	1,37
	AY	9	13		AY	9	12,32	125,95	0,68
	AW	10	29		AW	10	30,37	310,5	1,37
	Total		**100**		Total		**100,00**	1022,3	-
Mean value of discrepancy, %									**0,94**

Table 4—Results of quantitative determination of markers by a powder

Lab test results			Actual data on the commission of the customer				Discrepancy
Mixture	**Code**	**%**	**Mixture**	**Code**	**%**	**Mass, g**	**%**
1	1	31,00	1	1	27,03	2,16	3,97
	2	29,50		2	33,54	2,68	4,04
	3	-		3	-	-	-
	4	39,50		4	39,42	3,15	0,08
	5	-		5	-	-	-
	Total	**100,00**		Total	**100,00**	7,99	-
2	1	33,10	2	1	33,10	5,78	1,24
	2	20,20		2	20,20	3,42	0,12
	3	19,80		3	19,80	3,41	0,46
	4	-		4	-	-	-
	5	26,90		5	26,90	4,22	1,83
	Total	**100,00**		Total	**100,00**	16,83	-
3	1	8,20	3	1	8,20	1,11	1,07
	2	21,60		2	21,60	2,80	1,77
	3	42,10		3	42,10	3,77	10,63
	4	28,10		4	28,10	4,30	7,79
	5	-		5	-	-	-
	Total	**100,00**		Total	**100,00**	11,98	-
4	1	-	4	1	-	-	-
	2	27,50		2	27,50	3,02	3,63
	3	42,20		3	42,20	5,01	9,45
	4	-		4	-	-	-
	5	30,30		5	30,30	1,67	13,08
	Total	**100,00**		Total	**100,00**	9,70	-
5	1	32,10	5	1	32,10	5,01	6,17
	2	55,10		2	55,10	6,03	9,03
	3	-		3	-	-	-
	4	12,80		4	12,80	2,05	2,86
	5	-		5	-	-	-
	Total	**100,00**		Total	**100,00**	13,09	-
Mean value of discrepancy, %							**4,54**

The results of the tests carried out have determined:

1. In all sample mixtures, the signatures of the markers are correctly, 100%, determined;
2. The mean value of the discrepancy in testing with proppant was 0.94%, while testing with powder - 4.54%.

Both tests are recognized as successful by the customers.

Field results

We give two examples of the use of technology. In the first case, a well with a 5-stage MHD was investigated. Sampling was carried out from October 2017 to July 2018. It was revealed that during the monitoring period there was a redistribution of the efficiency of the well intervals: in the first months of the well, most likely, hydraulic fracturing was performed, and the well was put to the optimal mode (Fig. 15). Starting from April 2018, the fourth and fifth ports made a more pronounced contribution; in May 2018, a significant part of the oil inflow accounted for the fourth port, further, due to the rapid acquisition of data on the distribution of the inflow profile by July 2018, the inflow profile was equalized for therefore, move to a more rational exploitation of the well and more uniform formation of the reservoir.

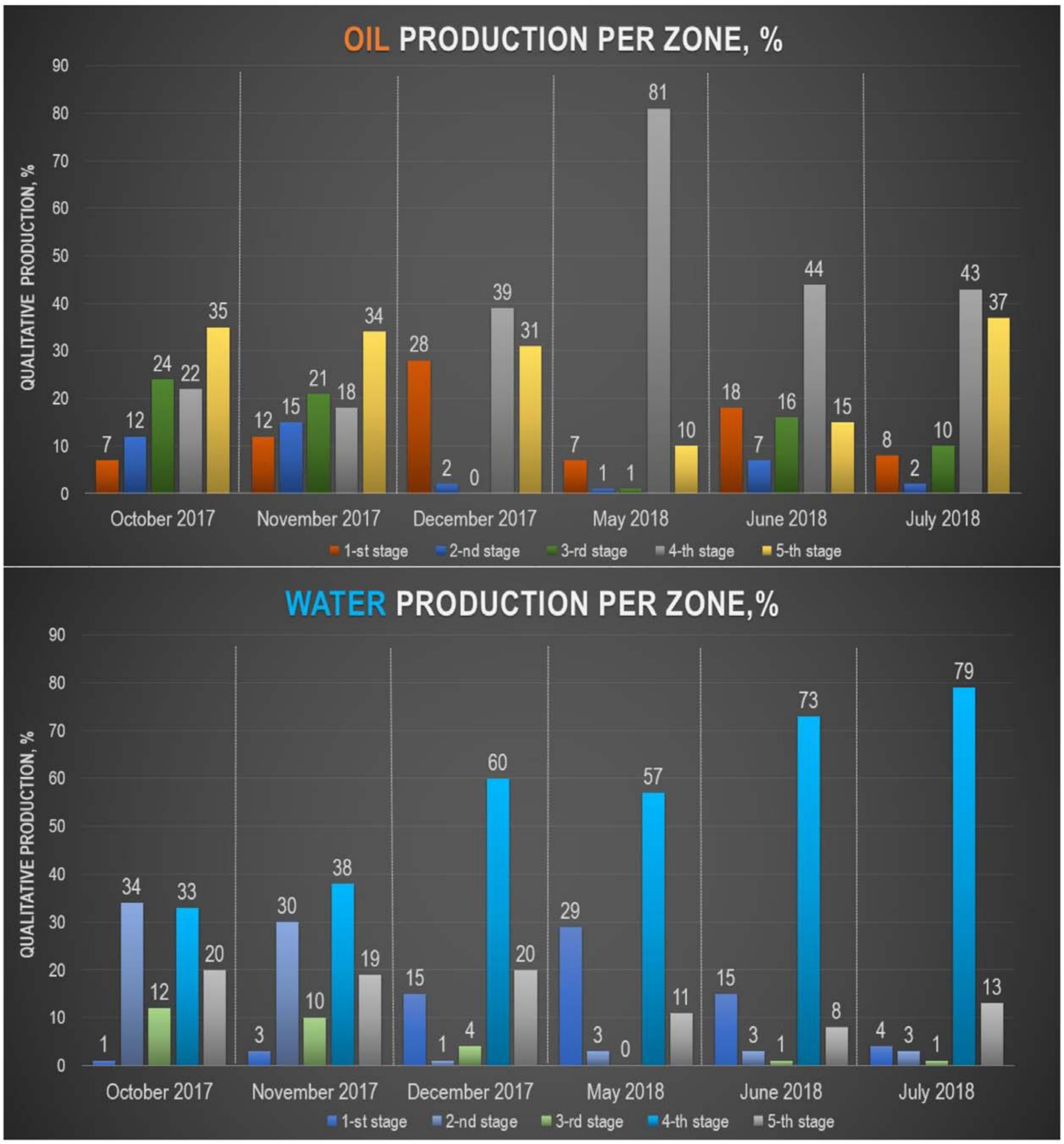

Figure 15—Dynamics of operation of the steps of a 5-stage stage multi-stage hydraulic fracturing unit for 6 months.

In the second case, four stages of the multi-stage hydraulic fracturing were carried out. The studies were conducted from September 2017 to July 2018 (Fig. 16). Since April 2018, there has been a significant redistribution of the flow profile - an increase in the flow rate of oil and water of the 4th port to 70% and a decrease in the flow through the 2nd and 3rd ports to a total of 13%. It was noted that during this period the dispersed state of the fluid changed - the free water in the presented samples was practically absent. May 2018, it is observed that almost the entire inflow of the horizontal wellbore for oil and water falls on the "heel of the well" - the 3rd and 4th ports, the total efficiency of which for water and for oil is 99%. The 1st and 2nd ports practically do not flow. Significant redistribution of the inflow profile may be associated with a change in filtration flows in the bottomhole formation zone and the withdrawal of the well to the regime.

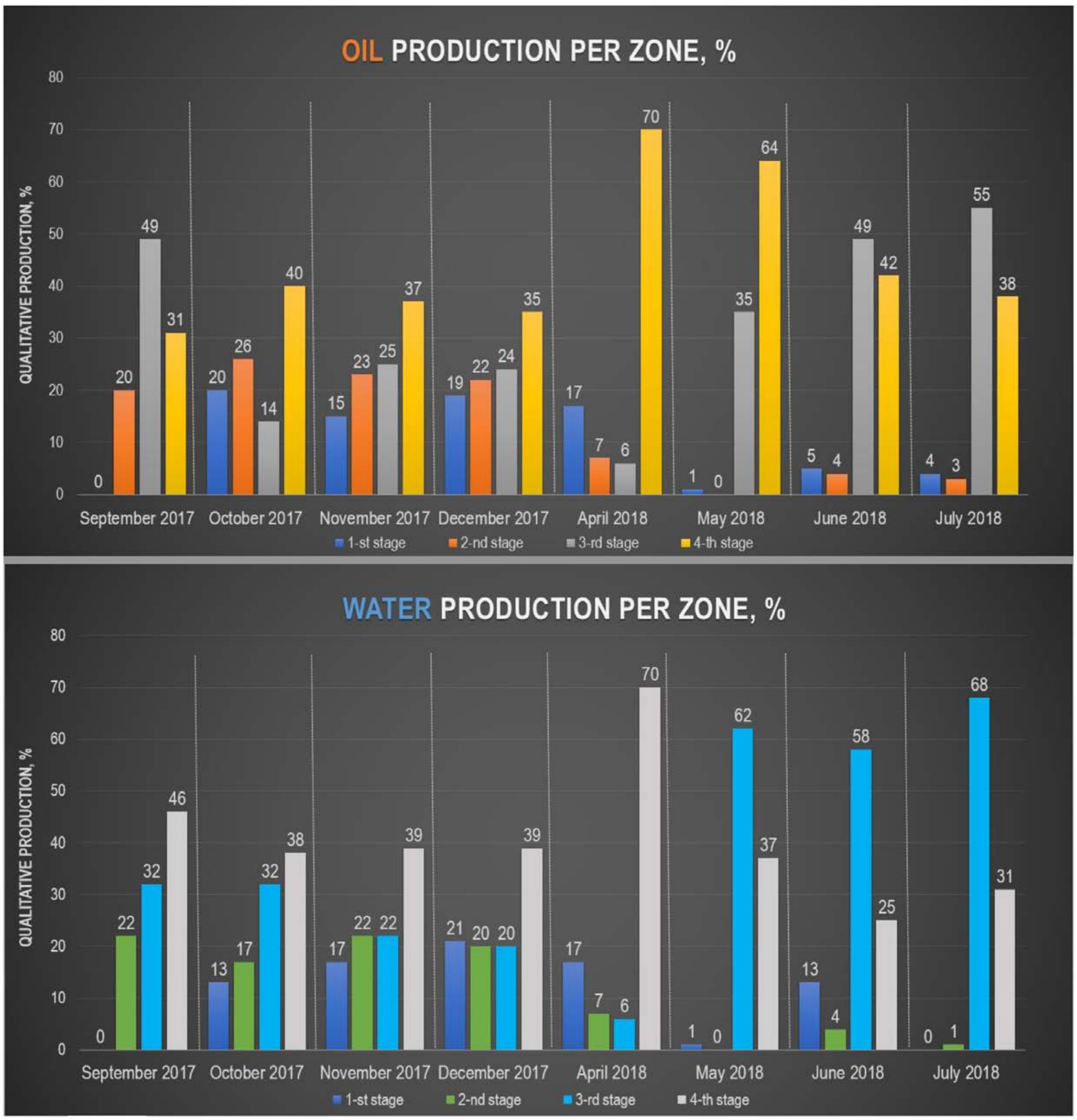

Figure 16—Dynamics of operation of the steps of 4-stage multi-stage multi-stage hydraulic fracturing for 8 months

Conclusion

However nowadays one of the most critical criterias in order to select proper production logging technique especially presented for most oil and gas production that is remaining could be named as operational and economical effectiveness. With whole variety of common technical and engineering solutions selecting proper one in order to minimize all possible risks is very important. There're many ways and Testing is the most important stage in making a decision for customers about the application of this or that tracer technology. The tests carried out by service company helped to answer many questions and additionally make sure the technology works well.

In our opinion, the O&G production companies should pay attention at the volume of tracer technologies tests conducted, which is a sign of how well the technology has been worked out. At the same time, a mandatory type of testing must be independent technology tests on the accuracy of the quantitative determination of tracers (markers), which can be claimed as mandatory for qualification of the contractor during the tender procedure.