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Application of Fluorescent Markers to Determine the Formation Fluid Inflow After MFrac

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Abstract

The primary objective of the technical development and underlying principles described in this article is the creation of physicochemical principles, of which the practical implementation allows users to quickly and accurately conduct production logging of horizontal wells after conducting multi-stage hydraulic fracturing.

The main physical phenomenon applied in the described method is the fluorescence of polymer microspheres – marker-reporters ranging in size from several hundred nanometers to several microns and containing quantum dots. Marker-reporters pass from synthesis and injection of proppant/sand into the polymer shell at our company's production facilities to high-precision instrumental determination of their concentration in formation fluid samples using flow cytofluorometry method in the laboratory. This method includes the following stages:

1. Synthesis of marker-reporters containing quantum dots
2. Preparation of polymer-coated proppant / sand with markers
3. Injection of the marked polymer-coated proppant / sand into the well during MFrac, followed by formation fluid filtration through it
4. Formation fluid sampling
5. Sample preparation for obtaining samples to be analyzed with the flow cytometer
6. Determination of marker-reporter concentrations in the samples by flow cytofluorometry data processing, also with our corporate software based on machine- learning principles

All the stages mentioned above are constantly being improved and optimized. The description of each stage of the relevant technological process is described below with a "historical reference" to the technological development behind it. The characteristics of the marked polymer-coated proppant Geosplit are also provided herein.

Marker-Reporter Synthesis and Obtaining Marked Polymer-Coated Proppant / Sand

Marker-reporters used for producing marked polymer-coated proppant /sand can have a different chemical nature. Accordingly, the methods of their synthesis are significantly different in the details, but have several common features, namely:

- The process of obtaining fluorescent marker-reporters is a polymer dispersion formation process (polymerization or polycondensation).
- The result of the dispersion process – marker-reporters being monodisperse organic or inorganic polymer microspheres consisting of a stabilized three-dimensional polymer (-network) containing colloidal quantum dots.
- Depending on the conditions of synthesis and subsequent processing of marker-reporters dispersion, the latter are either hydrophilic or oleophilic. This depends on the type of marked polymer-coated proppant/sand (hydrophilic or oleophilic) in which they will be applied.

During the process of synthesis, fluorescent substances (namely colloidal quantum dots) are introduced into the three-dimensional structure of marker-reporters. Several key features of quantum dots (fluorescent semiconductor nanocrystals) and their significant advantages over organic molecular fluorophores are presented below.

As the physical dimensions of the semiconductor particles decrease to nanometer scale (1-30 nm), these particles begin to exhibit properties that differ from bulk semiconductors. With this, we are talking about quantum-size effects. When a semiconductor nanocrystal interacts with electromagnetic radiation in the light range, an exciton is formed. An exciton is a hydrogen-like quasiparticle (electron and hole). The recombination of excitons, i.e. the process of "death" of the electron-hole pair in a semiconductor, leads to energy release. When the size of the exciton becomes comparable to the size of the nanocrystal, the electron levels occupy a strictly defined position or, in a different light, are quantized depending on the size of the nanocrystal. This is a quantum-size effect (Bergman, McHale, Taylor and Francis, 2012). Accordingly, by precisely controlling the size of the quantum dot, we can control the energy and hence the quantum dot fluorescence wavelength. That is, depending on the size, quantum dots will have a maximum fluorescence at different wavelengths.

Traditional organic fluorescent dyes are complex organic molecules, and they can oxidize, degrade or in some cases change their structure with relative ease. This, in turn, leads to deterioration or complete loss of fluorescent properties. Quantum dots are more durable and resistant to oxidizing agents. Optical absorption and fluorescence spectra for organic dye and quantum dots are presented on Figure 1.

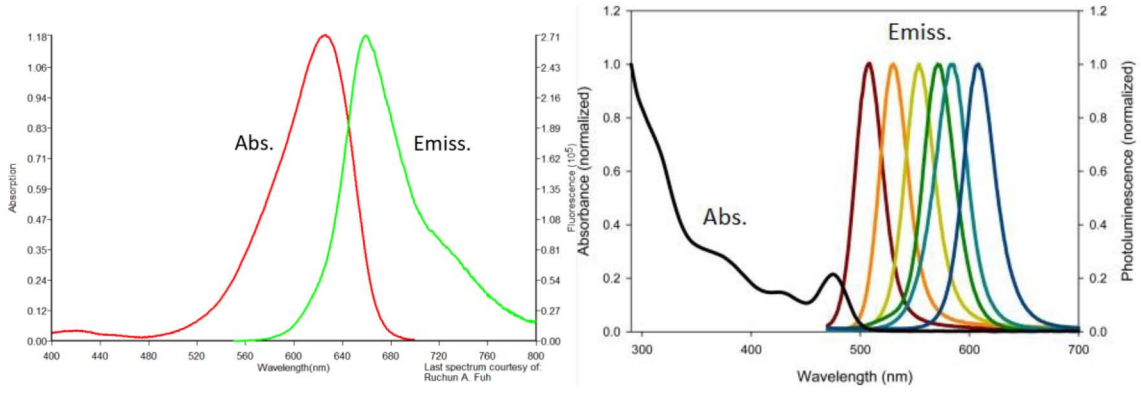

Figure 1—Optical absorption and fluorescence spectra for organic dye (left) and quantum dots (right)

Another advantage of quantum dots is the narrower fluorescence spectrum compared to dyes. Figure 1 displays the fluorescence spectra of a typical organic fluorophore and quantum dots. For organic dye fluorescence, the emission bandwidth at half-height is about 160 nm. At the same time, the emission bandwidth at half-height is about 40 nm for a quantum dot. This allows us to use a large coding capacitance in the visible light range compared to organic fluorophores, as well as to avoid overlapping spectra. This helps to improve the accuracy of the analysis.

Another competitive advantage of quantum dots is a wide range of fluorescence excitation compared to organic fluorophores. That is, a quantum dot can fluoresce with a high intensity when excited by light from ultraviolet radiation to its fluorescence wavelength, while the organic fluorophore must be excited by light in a narrow range of wavelengths.

The combination of the characteristic properties of quantum dots and their significant advantages over organic fluorophores provide key points for improved technology and allow us to achieve high accuracy in measurements.

As mentioned above, quantum dots ranging in size from 2 to 5 nm are placed inside insoluble polymer microspheres with a size of 1 micron (which is approximately 300 times more than quantum dots). Depending on the type of quantum dots inside the microsphere, it is possible to obtain different codes or, in other words, marker signatures. Utilizing combinations of 6 types of quantum dots allows for 63 different marker-reporter signatures.

Figure 2 presents real micrographs of markers Geosplit, which are microspheres about 1 micron in size. Figure 2 (on the right) shows a micrograph of one of the markers on the transmission electronic microscope. Here, the quantum dots are contrasting in homogeneities within the microsphere. Such insoluble microspheres that can fluoresce in different colors, depending on the type of quantum dots, are placed inside the proppant polymer coating, thus becoming the marked polymer-coated proppant Geosplit.

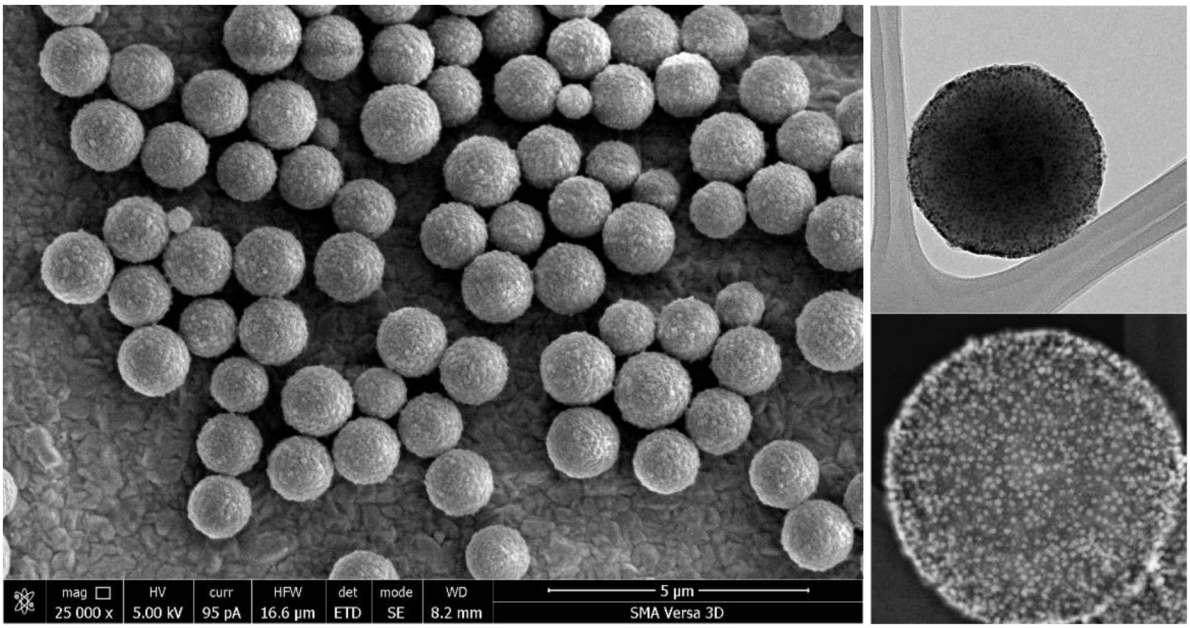

Figure 2—On the left - SEM micrograph of marker-reporters Geosplit (secondary electron detector), on the right - TEM micrograph of marker-reporters Geosplit

Initially, we used the so-called diphilic for the marker-reporters, i.e. having simultaneous affinity for both the water and hydrocarbon phases of the formation fluid. Even though these marker-reporters are more preferable from the point of view of synthesis, this technology may reduce the accuracy of determining their concentration at each phase of the formation fluid due to a number of reasons. In

this regard, we have developed a technology for separately obtaining marker-reporters based on their affinity to the corresponding formation fluid phase with resulting hydrophilic and hydrophobic marker-reporters. Hydrophilic marker-reporters cannot enter the hydrocarbon phase of the fluid, and vice versa, the hydrophobic marker-reporters cannot disperse in the water environment.

Figure 3 displays a schematic structure and a real micrograph of the polymer coating containing marker-reporters. One can select a solid insoluble polymer net among its components. This net protects the frame and is responsible for the strength characteristics of the composition. For the proppant, the strength of the coating is one of the key parameters. This insoluble net contains a functional polymer filler inside, in which the marker-reporters are dispersed. The main function of the filler is that, under the influence of the corresponding formation fluid phase, it swells and forms so-called diffusion channels that aid in transporting the marker-reporters from the inside of the proppant/sand polymer coating to the surface, followed by adsorption in the near-surface layer.

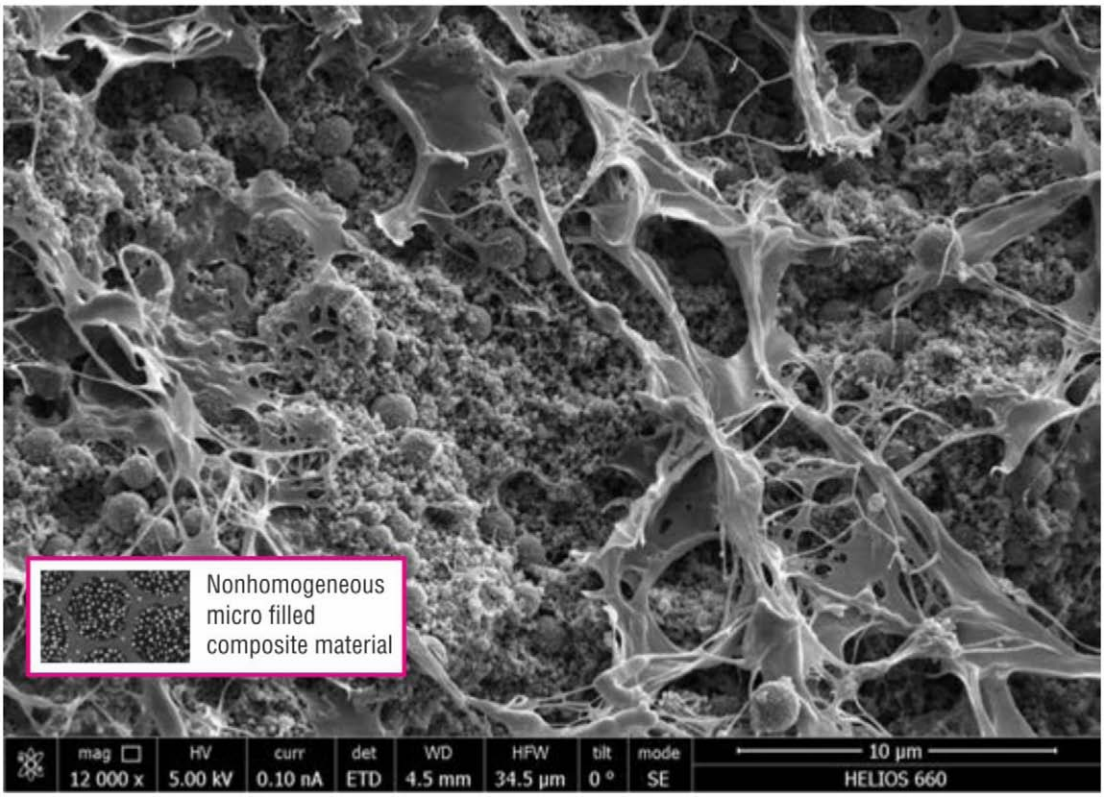

Figure 3—SEM polymer coating micrograph (secondary electron detector), insert – schematic structure of a polymer composite

As in the case of marker-reporters, a diphilic polymer coating, which is universal and can be wetted by water and oil formation fluid phases, may adversely affect the accuracy of determining the concentration of markers released under by the inflow. For the selective wetting and, accordingly, the selective separation of two types of marker-reporters in the corresponding formation fluid phase, we developed two types of the proppant polymer coating.

Depending on the chemical nature of the filler, the function of which is described above, the polymer coating can be either hydrophilic (wetted with water) or oleophilic (wetted with oil). Figure 4 shows a photograph of oleophilic proppant. Here, it can be seen that it is not wetted with water, while the hydrophilic proppant is thoroughly wetted with water. As a result, the oleophilic proppant allocates markers only in oil, and hydrophilic only in water. Due to the fact that water has a very large surface tension, the marker-reporters that are 1 micron in size are not capable of moving from one phase to another in reservoir conditions.

Therefore, we obtain a selective analysis for each formation fluid phase, thus improving the accuracy of the method.

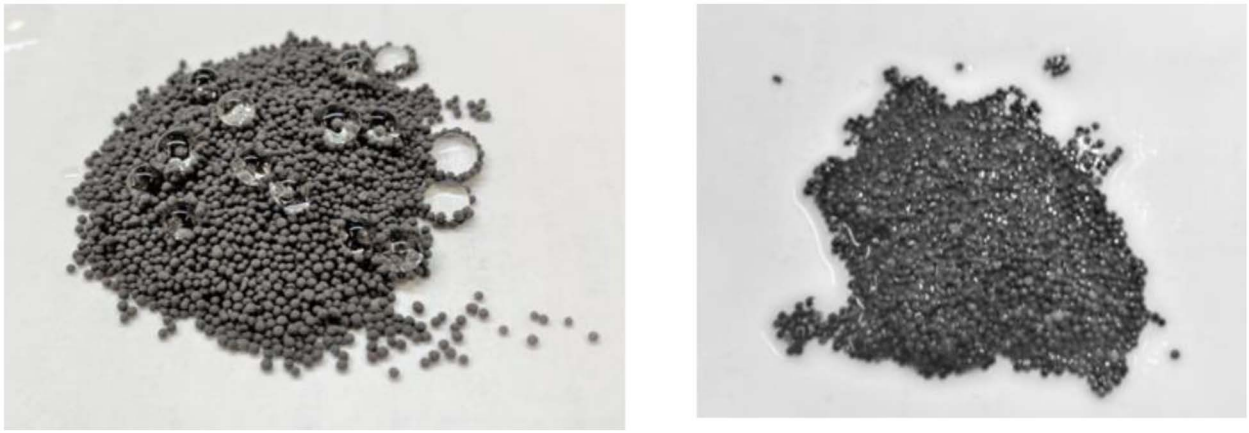

Figure 4—Photograph of oleophilic proppant (not wetted with water) – on the left, and hydrophilic proppant (wetted with water) – on the right

To briefly summarize the discussion above, quantum dots are placed in the bulk of insoluble micro-size marker-reporters, then injected into the polymer proppant / sand coating. Next, the marked proppant/sand is "pumped" into the well during multi-stage hydraulic fracturing. The 6 types of quantum dots allow for 63 different potential combinations, which inject their own unique code (signature) at each MFrac stage.

Markers are washed out from the coating under the influence of the formation fluid flow, after which they are injected into the formation fluid. These formation fluid samples are then later analyzed in the laboratory. Later, sample analysis is conducted in order to determine the concentration of marker-reporters coming from each interval of the production well.

Sample Preparation and Analysis

The analytical definition of marker-reporters is based on the instrumental method called flow cytofluorometry, or simply cytometry. This method is most often used in biology and medicine for the analysis of cellular substances (Greek Κτύος "cell"), which have linear dimensions close to marker-reporters. For reference, human erythrocytes are about 7 microns in size, and marker-reporters are about 1 micron (Shapiro, 2003). The principle of the cytometer's operation is as follows: the analyzed solution containing microspheres is mixed with auxiliary crimping fluid and, as a result of a finely tuned system of hydrodynamic focusing, all particles that were in the sample are lined up in a thin stream so that they can move in a row one after another. Next, they fall into the quartz cuvette compartment, where they are irradiated by lasers (there may be several of them). The fluorescence and light scattering signals for each particle after irradiation are recorded by appropriate detectors. In our case, the most informative channels are fluorescence channels in a different wavelength range. It should also be noted that marker-reporters are microspheres doped with quantum dots that can fluoresce in different colors depending on the signature number. After passing through the cuvette compartment, each such microsphere emits a dot in the 15-dimensional space of coordinates, but these dots can still be clearly identified. Figure 5 shows a cytometer that is used in our laboratory, along with examples of two-dimensional diagrams of pictured samples.

Figure 5—Photograph of a cytometer (on the left) and an example of a two-dimensional data diagram (on the right).

Flow cytometers work with aqueous and nearly aqueous solutions as a working medium. However, the real fluid is oil, a mixture of oil and water, an emulsion, which to all others may contain various impurities such as sand, clay, salts, gas bubbles, organic heterogeneities, etc. The laborious and time-consuming task is to isolate marker-reporters from the formation fluid in a sufficient quantity into the aquatic environment. To do this, we use the combination of various physical and chemical methods: selective filtration, centrifugation, dispersion, concentration and sorption. As a result of the sample preparation process, a small amount of pure liquid containing marker-reporters is obtained, which is necessary for further measurement using a cytometer.

After taking pictures, each marker-reporter represents a point in the 15-dimensional space of coordinates, making manual analysis of the data an extremely difficult task. The particular difficulty of this task is due to the presence of a large number of signals and marker-reporter codes in the analyzed sample. Moreover, errors resulting from the "human factor" cannot be completely eliminated with this approach.

To overcome these difficulties, we use an innovative data processing approach based on artificial intelligence (or machine-learning). The software, created by the company Geosplit, is based on machine-learning method using the "Random Forest" algorithm (Louppe, 2015). The principle of the operation can be simplified as follows: initially, the neural network is trained on "referee" samples of marker-reporters, from this the so-called "decision tree" is built. At each depth stage, parameters are sorted according to a certain parameter, for example, depending on whether the particle fluoresces with a green light or does not fluoresce. The depth of the tree can be varied. These trees, all with different structures, are created in a huge variety. As a result, when passing through such a tree, the marker of the desired code falls into a strictly defined "basket." Algorithms understand which basket each specific code should fall into using machine-learning. Then a mixture of a large number of markers is examined on the created tree and sorted. In other words, the algorithm considers how many markers of which type were in the mixture. Each tree makes its decision, or, relatively speaking, "votes" on the composition of the mixture. The use of formation fluids for training precisely from those proppants that were injected into the well allows for high accuracy in data interpretation. Machine-learning algorithms enable us to process a large array of data with a given accuracy in a short time frame and eliminate errors related to the "human factor".

Now let us briefly summarize the above-mentioned: the injected marked material identifies the markers. Markers, along with formation fluid samples, are then transferred to the laboratory, where they are cleaned and passed to the sample preparation stage. A clear mixture of markers obtained from formation fluid samples is analyzed using a cytometer. Data is then interpreted using machine-learning. As a result, we obtain the distribution of the marker code concentrations. These data are further used to build the inflow profiles for each multi-stage hydraulic fracturing stage.

Characteristics of the Marked Polymer-Coated Proppant Geosplit

The physical and chemical parameters of the marked semi-coated proppant Geosplit fractions 12/18, 16/20, 20/40 and 30/60 are listed in Table 1. Table 2 displays data on the conductivity and permeability of proppants of the same fractions according to the protocols obtained in the FracTech laboratory

Table 1—Physical and Chemical Indicators of Proppants

Physical and mechanical performance	Fraction, mesh			
	12/18	16/20	20/40	30/60
Bulk density, g / cm3	1,9	1,9	1,9	1,9
Specific weight, g / cm3	2,97	2,97	2,95	2,95
Sphericity	0,9	0,9	0,8	0,8
Roundness	0,8	0,8	0,8	0,8
Solubility in acid,%	2,0	2,3	3,9	5,1

Table 2—Conductivity and Permeability Indicators of Proppants

Pressure, PSI	Conductivity mDarcy / Foot		Permeability Darcy	
	16/20	16/20	16/20	30/60
2000	12038	2013	678	37,3
4000	9818	1755	572	59,1
6000	6969	1369	421	83,1
8000	3611	939	227	103
10000	1744	572	114	115

2lb/ft², 250°F, Ohio Sandstone

As can be seen from the data in Tables 1 and 2, the marked polymer-coated proppant Geosplit fully complies with the requirements of GOST R 51761-2013 to the proppants used for multi-stage hydraulic fracturing. Studies were conducted on the effects of hydrogen sulfide, the degree of proppant destruction, and the ability of the proppant to inject markers. Experiments on the effects of hydrogen sulfide were carried out using oil and water maximally saturated with hydrogen sulfide for 24 hours. During the experiment, it was shown that the proppant coating is chemically resistant to hydrogen sulfide. Also, the presence of hydrogen sulfide in the formation fluid does not affect the selection of markers from the proppant polymer coating.

There is a significant increase in the rate of marker release due to the destruction of the polymer coating, up to 21% of the destroyed fraction content, which significantly exceeds the requirements to the proppant according to GOST R 51761-2013. However, within 3-6 hours, the rate of marker release quickly returns to the stationary mode.

Conclusion

The method of using fluorescent marks described in this article for production logging after MFrac is the result of large-scale studies conducted in our company. This method has been patented in the Russian Federation (RF patent № 2018126690, 20.07.2018) and is currently undergoing the process of patenting abroad. Moreover, the method has been thoroughly tested in field conditions where its efficiency was

confirmed and found to be effective in wide applications for oil producing companies both in the Russian Federation and abroad.

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