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Assessment of the colloidal system with nanoparticles influence on wettability of carbonate rock surface

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ABSTRACT: The wettability of a surface of channels filtering liquids and gases under natural conditions of oil and gas reservoirs is one of the parameters that largely determines the filtration. A nature of the filtration channel surface wettability determines a phase permeability, capillary forces and intensity of adsorption at the interface. An ability of the filtration channel surface to be wet by the polar or nonpolar phases of formation fluid and process liquids affects the filtration-capacitive parameters of oil and gas saturated rocks. In this regard, in the development of oil and gas fields, much attention is paid to the study of physicochemical phenomena and processes occurring at the interfaces. An article presents the results of a set of laboratory experiments to study the surface activity of the colloidal system in the form of an emulsion with supercharged nanoparticles. A set of filtration experiments was carried out using the United States Bureau of Mines (USBM) method in order to assess an effect of the emulsion system with nanoparticles on wettability of the surface of oil and gas reservoir rock filtration channels. The research was conducted on rock cores of two oil and gas fields in the Ural-Volga region of the Russian Federation. According to the applied experimental procedure, rock cores were preliminarily maintained under reservoir conditions to give a surface of pore channels the properties close to the natural conditions. After that, the wettability of rocks was assessed by measuring the USBM wettability index before and after filtering the emulsion system with nanoparticles. Analysis of the research results showed that filtration of the emulsion system with high surface activity led to a change in the wettability of rocks from completely hydrophilic (USBM index – 0.60) to completely hydrophobic (USBM index – minus 0.32). The research results allowed to conclude that there is a high potential for application of emulsion systems with supercharged nanoparticles to control the filtration of formation fluids and process liquids in natural oil and gas reservoirs.

KEYWORDS: nanoparticles; silicon dioxide; emulsion system; wettability; carbonates; USBM index

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INTRODUCTION

A quality of hydrocarbon reserves development, as well as an effectiveness of methods of technogenic impact on natural reservoirs of oil and gas are largely defined by correctness and relevance of information about a wettability of surface of filtration channels. Determination of the wettability of surfaces in a natural reservoir system is a non-trivial task. In solving this task, it is recommended to take into account in complex a natural geological, physicochemical phenomena and processes occurring at macro and micro levels of the filtration channels, as well as a geological transformation and change in thermobaric conditions of reservoirs initiated by an anthropogenic impact [1–8]. At a stage of geological development of oil and gas reservoir, the wettability of rock surface is defined by the properties of minerals composing a rock, and surface changes in dynamics depending on geological transformations and properties of multicomponent reservoir fluids, which saturated the reservoir. As a result of an adsorption of reservoir fluid molecules on a surface of the pore channels, a film of positively or negatively charged fluid is created, which defines the wettability of the pore channel surface. In the process of development of oil and gas reservoir, the wettability will change along with a change in the properties of reservoir fluids due to a violation of thermobaric equilibrium of the reservoir system, as well as filtration of technological agents in the reservoir. A large number of experimental methods for studying the wettability of rock surfaces were developed in the second half of the 20th century [9–17]. One of these methods is the United States Bureau of Mines (USBM) method, according to which a wettability of rocks is assessed by a hysteresis loop of capillary pressure curves [5, 9]. This technique was used by the authors of this article for experimental research and assessment of colloidal systems with nanoparticles influence on the wettability of rock surfaces of two oil and gas fields in the Volga-Ural oil and gas province.

METHODS AND MATERIALS

As a part of preparatory work for the experiments, the rock cores of geological objects Bashkir (SBASh) and Turney (S_{Tur}) of two oil and gas fields of the Volga-Ural oil and gas province were selected and studied. Preparation of core material for the research was carried out in accordance with the requirements of industry and state standards [18–20].

In order to conduct experiments in conditions closest to natural, laboratory experiments simulated the natural reservoir conditions of the studied geological objects. As models of reservoir fluids, oil samples were used, taken from wells drilled in geological objects under study S_{BASh} and S_{Tur}. A brief geological and physical characteristics of the geological objects is given in table 1.

Oil samples were placed in a metal container made of stainless steel and heated to a temperature exceeding the reservoir on 20°C. At this temperature, the oil was kept for 3 hours with periodic stirring. Next, it was cooled to reservoir temperature and filtered through a porous medium. The sample of oil was considered suitable for experiments if the filtration did not attenuate while passing through a cylindrical core sample. Then, the density and viscosity of the obtained oil sample were determined at reservoir temperature. In order to simulate the residual water saturation of rock core samples, a reservoir water model prepared using calcium chloride was used.

To conduct research, six cylindrical core samples were taken from the wells of S_{BASh} and S_{Tur} geological objects. A brief filtration-capacitive characteristic of the core samples is presented in table 2.

At the stage of preparation of process liquids for experiments, laboratory samples of the emulsion system with silicon dioxide nanoparticles (ESN) were prepared. The colloidal system ESN is industrially used as a water-limiting or oil-displacing agent in technologies for intensifying oil production or enhancing oil recovery [21–30]. The nanoparticles used in the experiments are ultra-hydrophobic. The concentration of solid and aqueous phases of the ESN sample was 0.5 and 81.5% vol. respectively.

The assessment of a wettability of rock surface was carried out according to the U.S. Bureau of Mines (USBM) method developed by Donaldson et al. [5, 9]. This tech-

Table 1

A brief geological and physical characteristics of the geological objects S_{BASh} and S_{Tur}

Name	Object S_{BASh}	Object S_{Tur}
The average depth of the roof, m	1100	1450
Rock	limestones with interlayers of dolomites	dolomitic limestones
Type of porosity	cavernous-fissure	mixed
Porosity coefficient, frac.	0.13	0.10
Oil saturation coefficient, frac.	0.80	0.68
Permeability, 10^{-3} μm²	47.0	21.0
Initial reservoir temperature, °C	22.0	27.0
Viscosity of oil in reservoir conditions, mPa • s	12.4	10.2
Density of oil at reservoir temperature, kg/m³	880	860
Viscosity of water at reservoir temperature, mPa • s	1.29	1.38
Density of water at surface conditions, kg/m³	1108	1125

Table 2

A brief filtration-capacitive characteristic of the rock core samples from the wells of S_{BASh} and S_{Tur} geological objects

Geological objects	Rock core number	Porosity (gas), frac.	Permeability (gas), 10^{-3} μm^2
S_{BASh}	1	0.20	13.4
	2	0.17	59.7
	3	0.14	6.9
S_{Tur}	4	0.12	12.2
	5	0.10	8.0
	6	0.13	11.6

nique is based on the assessment of wettability by a hysteresis loop of capillary pressure curves [5, 9–12]. Capillary pressure curves were obtained by alternately displacing water and oil from core samples using a centrifuge. The method for determining a preferential wettability of rocks is based on a comparison of the amount of work necessary for one liquid to displace another. The areas limited by the capillary pressure curve and the abscissa axis between the two fluids saturation limit values are a measure of the work that needs to be expended to displace the corresponding fluid from the sample. Less energy is required to displace the non-wetting phase by the wetting phase, than to displace the wetting phase by the non-wetting phase. Therefore, the ratio of areas bounded by capillary pressure curves is a direct indicator of the degree of wettability. The decimal logarithm of the ratio of area corresponding to the case of water displacement by oil (A_1) to the area corresponding to the case of oil displacement by water (A_2) is used as an indicator of wettability and is called an index of preferential wettability I_{USBM} [5, 9].

The preferential wettability index USBM is calculated as the logarithm of the area ratio according to the capillary pressure curves:

$$I_{USBM} = \log_{10} \cdot [A_1]/[A_2],$$

where A_1, A_2 – capillary pressure curve areas.

An increase in positive values to $+\infty$ indicates an increasing preferential wetting of a surface with water to infinite hydrophilicity. Zero value characterizes equal wetting of a surface with both fluids (neutral wettability). An increase in negative values to $-\infty$ indicates an increasing preferential wetting of a surface by oil to infinite hydrophobicity [5, 9].

An order of the experiment is as following:

1) Place the samples saturated by water (with residual oil saturation) in centrifuge glasses and filled them with oil so that it covered the core.

2) Launch the centrifuge, stepwise increasing the rotor speed. At each subsequent increment of the rotation speed, the amount of water displaced from the sample was measured. Samples were rotated at each stage for 12 hours to achieve hydrostatic equilibrium.

3) After the rotor is stopped, the samples were weighed and extracted in a Sachs apparatus.

Two main stages could be distinguished in the carried out experimental research, which were a determination of wettability of the rock surface before and after filtration of ESN.

At the first stage of the research, experiments were conducted to determine a wettability of rock samples and to calculate the wettability indices, which were taken as the initial ones for further comparative analysis and evaluation. The wettability indices of rock core samples were determined according to the procedure consisted of two sequential cycles:

– From the water-saturated samples, a water was displaced by oil using a centrifuge. At each centrifugation stage, the amount of displaced water was recorded to calculate the coefficient of residual water saturation. Next, from samples saturated predominantly with oil, the oil was displaced by water using a centrifuge. At each centrifugation stage, the amount of the displaced oil was recorded to calculate the coefficient of residual water saturation. As a result, the dependences of the water saturation coefficient of rock samples on capillary pressure were obtained ("capillary imbibition" curve).

– From the predominantly water-saturated samples, a water was displaced by oil using a centrifuge. At each centrifugation stage, the amount of displaced water was recorded to calculate the coefficient of residual water saturation. As a result, the dependences of the water saturation coefficient on capillary pressure were obtained (curve of "secondary drainage").

At the second stage of the research, a similar set of experiments and calculations was performed, but after filtering the ESN in rock core samples.

RESULTS

In accordance with the methodology presented above, the filtration experiments were carried out to determine

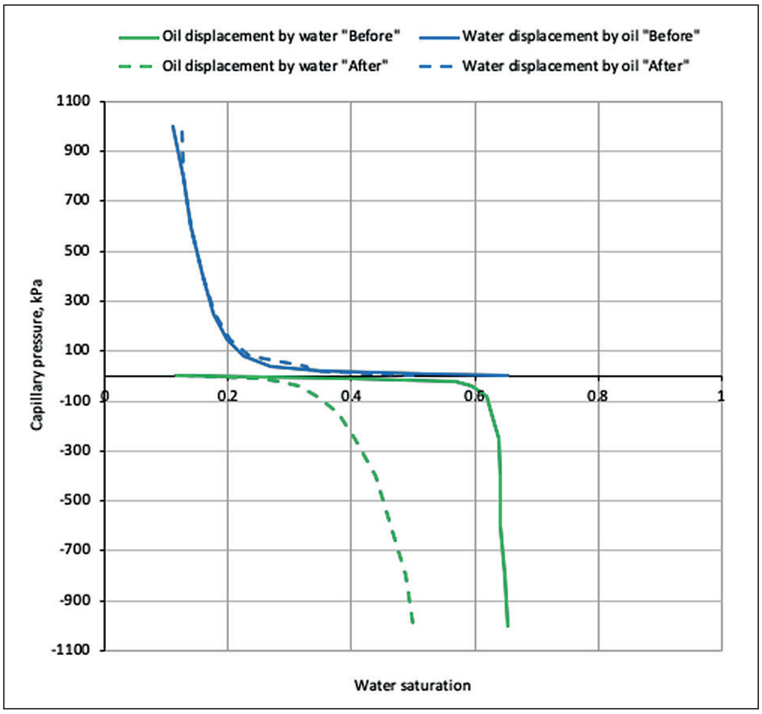

Fig. 1. **Capillary pressure curves for the rock core sample No. 2 of the geological object S_{BASh} before and after filtration of ESN**

an intensity of the ESN influence on the wettability of the filtration channels of carbonate rock core samples from geological objects SBASh and STur. The content of silicon dioxide nanoparticles in the ESN sample was 0.5% vol. when the content of the aqueous phase is 81.5% vol. The results of the experiments with obtained capillary pressure curves and the wettability indices for the core samples No. 2 and 5 are presented in Fig. 1–4.

The results of experiments graphically presented in Fig. 1 illustrate a significant decrease in capillary pressure for the displacement of oil by water after filtration of a colloidal system with nanoparticles ESN in a rock core No. 2. At the same time, there was no significant change in the capillary pressure curve for the process of water displacement by oil, which is an ambiguous result. Based on the obtained capillary pressure curves, the wettability indices USBM were calculated (Fig. 2).

The results of calculations of wettability indices by the USBM method, graphically presented in Fig. 2 showed that colloidal systems with nanoparticles ESN significantly impacted on the wettability of carbonate rocks and made it possible to change the wettability index USBM from 0.67 (hydrophilic surface) to minus 0.12 (hydrophobic surface).

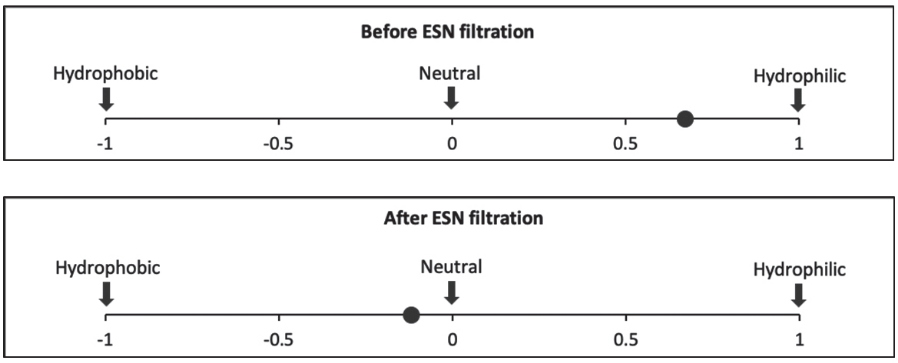

Fig. 2. **Wettability indices USBM for the rock core sample No. 2 of the geological object S_{BASh} before and after filtration of ESN**

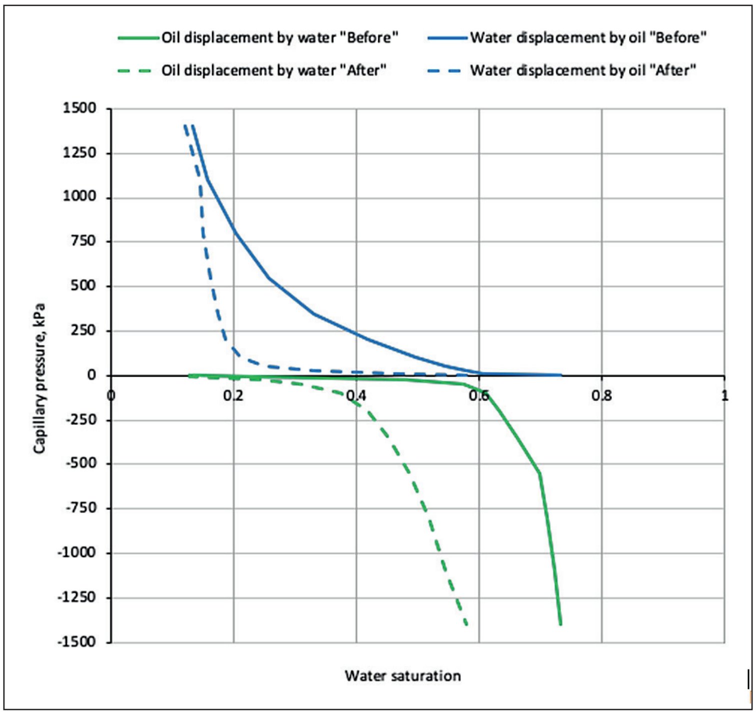

Fig. 3. **Capillary pressure curves for the rock core sample No. 5 of the geological object S_{Tur} before and after filtration of ESN**

The results of experiments graphically presented in Fig. 3 showed that filtration of the colloidal system with nanoparticles ESN in a rock core No. 5 drastically impacted on the capillary pressure curves for both water displacement by oil and oil displacement by water. In these experiments the filtration of the ESN decreased capillary pressure for displacement water by oil and oil by water, which is not correlated with theoretical understanding of the dependence between preferential wettability of rock surface and efficiency of the displacement process. Based on the obtained capillary pressure curves, the wettability indices USBM were calculated (Fig. 4).

The results of calculations of wettability indices by the USBM method, graphically presented in Fig. 4 showed that colloidal system with nanoparticles ESN significantly impacted on the wettability of the rock surface, providing the possibility to change the wettability index USBM from 0.60 (hydrophilic surface) to minus 0.32 (hydrophobic surface).

A comparative assessment of the ESN influence on the wettability index of carbonate rocks is given in Table 3 and in Fig. 5.

According to the results of filtration experiments, it was found that the filtration of the colloidal system ESN

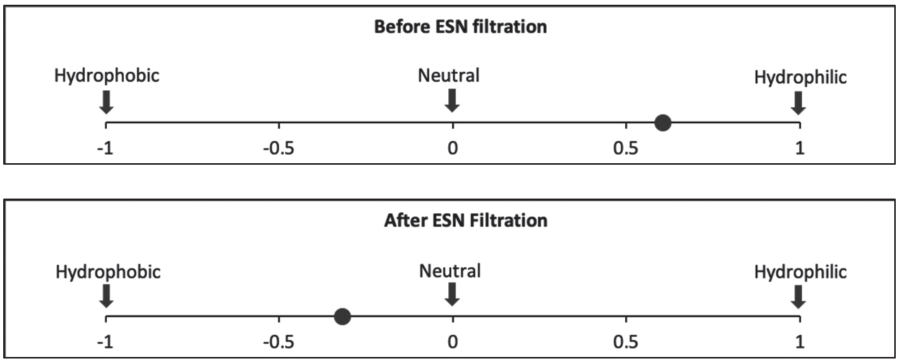

Fig. 4. **Wettability indices USBM for the rock core sample No. 5 of the geological object S_{Tur} before and after filtration of ESN**

Table 3

Wettability of the rock surface of geological objects S_{BASh} and S_{Tur} before and after filtration of ESN

Geological object	Rock core number	Wettability index I_{USBM}	
		Before filtration of ESN	After filtration of ESN
S_{BASh}	1	0.76	0.19
	2	0.67	–0.12
	3	0.74	0.19
S_{Tur}	4	0.21	–0.02
	5	0.60	–0.32
	6	0.11	–0.17

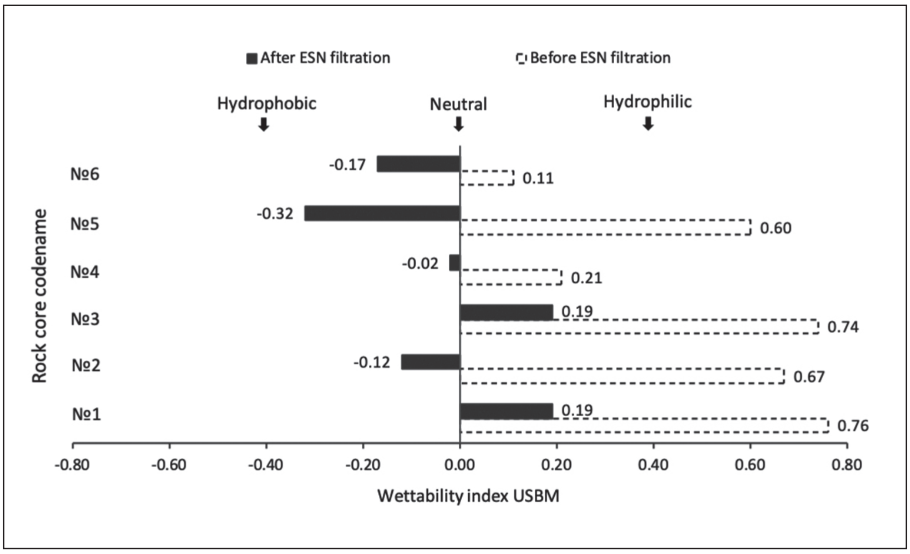

Fig. 5. **The wettability index of the rock surface before and after filtration of ESN**

in cores of carbonate rocks with a predominant hydrophilicity of the surface of the pore channels led to a decrease in the degree of hydrophilicity or an absolute change in the wettability of the surface of filtration channels (Fig. 5). For core samples No. 1 and 3, a decrease in the levels of hydrophilicity were recorded from 0.76 and 0.74 to 0.19 for both samples (an average decrease of USBM index for two samples was 0.56). More significant changes were observed in the experiments with core samples No. 2, 4, 5, and 6, where all initially hydrophilic samples become hydrophobic. The highest decrease of USBM index from 0.60 (completely hydrophilic surface) to a minus 0.32 (completely hydrophobic surface) was recorded for the sample No. 5. An average value of USBM index for six core samples under study before filtration of ESN was 0.52 (completely hydrophilic), after filtration of ESN minus 0.04 (neutral).

CONCLUSION

The results of a series of laboratory experiments to study the effect of colloidal systems with nanoparticles influence on the wettability of rock filtration channels showed a high technological functionality of ESN to control the wettability of the surfaces of fluid-saturated fractured-porous rocks. An analysis of the research results showed that the filtration of ESN in rock cores of oil and gas fields of the Volga-Ural oil and gas province in four of six experiments led to an absolute change of rock surface wettability from completely hydrophilic to completely hydrophobic. The highest level of surface wettability change assessed through USBM index was recorded for sample No. 5, where USBM index decreased from 0.60 to minus 0.32. For petroleum engineers, the ability to control a wettability of rocks is a highly effective mechanism to control the development of the oil and gas reservoir, because an alteration of rock surface wettability for filtrating oil-gas-water mixtures allows to alter a direction of filtration flows in the bottom hole zone. Alteration of wettability of rock filtration channels is an efficient lever for influencing phenomena such as interfacial tension, capillary pressure and capillary imbibition, which in turn determine the rate and completeness of oil and gas recovery. The results of conducted experiments indicated a great promise of use colloidal systems with supercharged silicon dioxide nanoparticles to control the filtration of liquids through oil and gas saturated porous-fractured media.

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