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Study on application of colloidal particles of metal oxides to increase the oil recovery factor

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Abstract. The extraction of heavy oil, including bitumen, is complicated by the extremely high viscosity of the fluid in the reservoir. The adsorption of heavy oil fractions on the surface of minerals leads to the hydrophobization of the pore space. The magnetic colloidal particles of iron oxides present in the composition of the water remove adsorbed oil from the surface of pores, which manifests itself as an increase in the oil recovery factor and the injectivity of injection wells. Iron particles of submicron size, located on the surface of an electrically charged gas bubble, are concentrated at the water-oil interface. Due to the high adsorption energy on the surface of the iron particle, oil is deposited on the iron oxide particles. The drop-in bottom pressure of injection and production wells contributes to the movement of the gas bubble with oil and iron oxides to the bottom of production wells. The study of the mechanism of exposure to electromagnetic radiation showed that the electromagnetic field selectively heats the particles of iron oxide, causing catalytic cracking of oil, and contributes to an increase in the oil recovery factor and well productivity index.

1. Introduction

Interest in the use of nanotechnology in the development of oil and gas fields is growing. Traditional methods, such as nuclear magnetic logging and indicator injection, do not provide reliable information on the distribution of residual oil in the reservoir. Development of heavy oil fields by using aqueous solutions is complicated by the high viscosity of the oil and gas fluid in the oil reservoir [1-8]. In addition, adsorption of asphaltenes and resins on the surface of minerals leads to hydrophobization of the pore space, which also prevents the process of oil displacement.

Ferrofluid (or magnetic fluid) is a stable dispersion of paramagnetic nanoparticles, coated with a dispersant, in a liquid carrier. These magnetic particles can be magnetized and have sizes from 3 to 15 nanometers. The behavior of the magnetic fluid depends on the presence or absence of a magnetic field. The suspension is stable as the dispersant prevents agglomeration of the particles and the Brownian motion keeps the particles in the carrier fluid. Ferrofluid can be injected into oil fields without the significant decreasing of permeability. Surface-coated nanoparticles are able to penetrate through micron-sized pores over long distances in the reservoir with small losses of nanoparticles in the rock. Nanoparticles change the magnetic permeability of the flooded area of the field. Paramagnetic particles are particles that are oriented parallel to the applied magnetic field and do not retain the magnetic moment after the field is removed, i.e. soft magnetic particles. The mass force acting on the liquid is due only to the magnetic polarization of the particles. Paramagnetic nanoparticles retain their mobility in intense magnetic fields. While a liquid with paramagnetic particles of micron size or more solidifies

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in the presence of an applied magnetic field. Paramagnetic nanoparticles have unique properties. Ferrofluids can be easily filtered in the pore space of the formation. The properties of paramagnetic nanoparticles depend on their size due to the large ratio of surface area to volume of nanoparticles. Ferrofluids can be designed in such a way that they have certain magnetic and interfacial properties (long-term dispersion stability in an aqueous solution with minimal losses in the reservoir and adsorption at the interface of the oil-water phases). Paramagnetic nanoparticles are either adsorbed at the oil-water interface or dispersed in one of the two liquid phases coexisting in pores of the reservoir rock [9-13].

The magnetization of the ferrofluid is easily controlled. Stable water dispersions of paramagnetic nanoparticles moving under the influence of the applied magnetic field can be potentially useful for monitoring the process of field development. The interfacial tension acts as a restoring force, which increases the interphase oscillations and phase pressures, which helps to detect the location of the phase boundary, determine the distribution of multiphase fluids in the reservoir rock and the location of the lenses with residual oil. There is a potential application of the method of injection of aqueous solutions of ferrofluid as Improved Oil Recovery (IOR) and Enhanced Oil Recovery (EOR) methods for mature, heavy oil, High Pressure High Temperature and highly water saturated fields [9-11, 14-19].

Magnetic pressure depends on the pore geometry, the strength and direction of the magnetic field. The magnetic pressure created by the magnetization of the wetting phase helps to displace the fractal aggregates (or ganglia) of the non-wetting oil and thereby reduce the residual oil saturation. Magnetic stresses are amplified near the contacts between the fractal aggregates of oil and the wall of the rock matrix twice. Fractal aggregates of oil have a tendency to adapt to the configuration of the voltage by disconnecting it from the walls of the matrix of rock. Stresses caused by magnetization of ferrofluid can help overcome strong capillary pressures and displace fractal aggregates of residual oil [13].

Monitoring the movement of reservoir fluids in a porous medium can be based on inter-well electromagnetic (EM) conductivity monitoring technology. Reservoir fluids and injected water have different magnetic permeability. Magnetic response or sensitivity of inductive measurements from heterogeneous fluids is best detected at high frequencies. As the injected slug of ferrofluid moves through the reservoir, the dispersion leads to a decrease in the concentration of nanoparticles, and the spatial contributions of magnetic measurements become more scattered [11].

The effect of the magnetic field on paramagnetic nanoparticles leads to an increase in the velocity of their motion in liquid phases and to a shift in the phase boundary. Measurements of the interfacial motion between an aqueous solution of paramagnetic nanofluid and a non-magnetic fluid using phase-sensitive optical coherence tomography showed a doubling of frequency and magnetic susceptibility. The application of an innovative method of magnetic resonance imaging (MRI) using paramagnetic nanoparticles makes it possible to improve the accuracy of determining the location of residual oil in the reservoir. The new method is based on the concept of detecting the acoustic response (and resonance) of the interface between oil and ferrofluid in the porous space of rock exposed to an oscillating magnetic field [12, 19].

The objective of this article is to increase the injectivity of wells due to the magnetic field treatment of working agents represented by aqueous solutions of colloidal particles of iron oxides.

2. Study of the influence of colloidal magnetic particles of iron oxides on the process of oil displacement

The study of water displacing properties showed that in addition to temperature, impurities of colloidal magnetic particles of iron oxides in water play a huge role in the process of oil displacement. Superparamagnetic iron oxides magnetic particles image were really registered in oil by using Transmission Electronic Microscopy (TEM) technique [20, 21]. Electronic Magnetic Resonance (EMR) studies of water and oil have also shown the presence of nano-sized superparamagnetic iron oxide particles in water and oil [20, 22 and 23].

In articles [20, 21] the characteristic sizes of such particles in oil were determined by Transmission Electronic Microscopy (TEM): length 50-100 nm, diameter 10-20 nm. Superparamagnetic particles form aggregates of fractal structure (FA) of sufficiently large size: 10^3 -10^5 nm. Studies of tap water by

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Electronic Magnetic Resonance (EMR) method showed the presence of such particles: in the EMR spectrum, the presence of nanoparticles with a characteristic size of about 10 nm is recorded as a single line with g factor 2, 186 (+/- 0.003) and a width ΔH=70 Oe.

In Figure 1, an image of a superparamagnetic magnetite/maghemite particle (a rod-like particle) as part of an aggregate of colloidal oil particles (rounded gray particles) is presented. The image was obtained by high resolution of Transmission Electronic Microscopy (TEM) method.

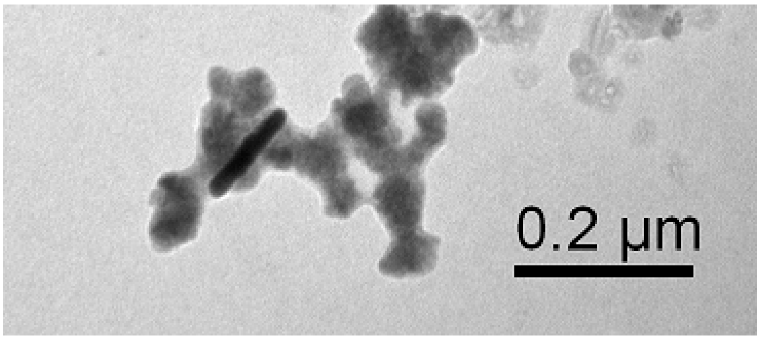

Figure 1. Superparamagnetic particle of iron oxide (rod like particle) as part of the unit of colloidal oil particles aggregate.

In articles [21, 24], it was shown that the treatment of water by flowing through a pipeline, inside which a magnetic field is specially formed, leads to the destruction (crushing) of magnetic particle aggregates. To establish this fact, water filtration through a filter with a pore size of 2-3 microns was used. It was found that after magnetic treatment of water, the amount of iron particles retained by the filter decreased more than twice. Magnetically untreated retained particles Electronic Magnetic Resonance (EMR) spectrum contained line with g = 2,186, however, in the treated retained EMR spectrum this line were absent. Thus, in the spectrum, EMR has disappeared line of particles of small size, i.e. FA fragmentation occurred, as a result of which fragments of the initial aggregates of fractal structure (FA) and small particles were able to pass through pores with a diameter of 2-3 microns.

In the EMR spectra of both treated and untreated iron particles, narrow (less than 5 Oe wide) single lines were found that correspond to organic radicals adsorbed on the particles. Further studies have shown that upon contact of water with air, gas bubbles of a wide range of diameters from 10 to 100 nm are formed on iron oxide particles [21].

In article [25], the presence of electric charges on the surface of gas bubbles - bubstone, the size of about 100 – 200 nm in electrolyte aqueous solutions of was established. Bubstones form aggregates of fractal structure, consisting of tens - hundreds of microbubbles. The presence of an electrically charged surface prevents these bubbles from collapsing even at pressures of several tens of atmospheres, which allows them to migrate in the porous space of the formation, interacting with electrically active heavy components of oil.

It is known that the adsorption energy of asphaltenes and resins on the surface of magnetic particles of iron oxides exceeds the energy of their intermolecular attraction, which allows, for example, to purify water emulsions from oil impurities [26]. In article [24], it is shown that the magnetic colloidal iron oxide particles present in the composition of water remove adsorbed oil from the pore surface, which is manifested as an increase in the extraction coefficient and an increase in the pickup of injection wells. This effect occurs due to the fact that iron particles of submicron size located on the surface of an electrically charged gas bubble are concentrated at the water-oil interface. Due to the high adsorption energy on the surface of the iron particle, oil is deposited on the iron oxide particles, and due to the gas bubble is involved in the process of movement.

Summing up the above, it can be argued that the role of impurities of nanoscale magnetic iron oxides in water is to form flotation (washing) components representing FA and colloidal particles that are part of gas bubbles (or the surface of gas bubbles). Such a gas bubble, located at the water-oil interface,

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collides with a colloidal particle of oil, adsorbs it in its volume and is filtered together with the water flow.

As noted above, colloidal particles and their aggregates of FA are usually present in water in concentrations of the order of units – tens of grams per ton. For example, in purified tap water, which was studied in [22, 24], the total concentration of iron atoms was approx. 0.3 g/ tone. With this concentration, the sizes of the significant part of FA was greater than 3 microns. The large size of aggregates of FA particles of iron oxides present as micro-impurities in water, prevent the penetration of FA into the pores of small size, reducing the coverage of the formation by the action of iron oxides. Treatment of water by a magnetic field makes it possible to split such aggregates of FA into smaller particles capable of penetrating into pores of small size, providing an increase the rate of the water flooding in injection wells. It should be noted that the addition of magnetic iron nanoparticles in oil is accompanied by a decrease in its viscosity by tens of percent [14]. The penetration of iron nanoparticles in oil helps to increase the efficiency of water flooding.

The presence of iron impurities in water sources allows to increase the concentration of nanoscale magnetic particles of iron oxides by magnetic treatment of water, without the introduction of particles. Industrial tests of magnetic devices were carried out at the field of the Republic of Tatarstan. Installation of magnetic devices on two water injection wells with a injection index of about 200-300 cubic meters per hour allowed to increase the average annual pick-up rate of wells for fresh water by about 110%, and for salt water – by 40%. The growth effect developed within 2-3 months. Industrial tests of magnetic devices were carried out at the field of the Republic of Tatarstan.

Experiments on the displacement of oil by water with metal oxide particles are interpreted as a manifestation of a decrease in surface tension energy at the oil/water boundary [17]. This interpretation does not contradict the proposed mechanism of action of the complex particle – iron oxide + gas bubble.

Indeed, thanks to the electric charge, such a particle will experience the forces of attraction to water, which has a high dielectric permeability and electrical conductivity. Due to adsorption of oil particles, the oil/water boundary changes to the water/rock boundary. Because the rock pore surface is covered by an adsorbed layer of water, the apparent surface tension energy of water/oil is reduced.

The properties of natural impurities of metal oxide nanoparticles to reduce the energy of surface tension and reduce viscosity [14, 17] led to intensive studies of the effect of artificial introduction of impurities of various metal oxides, including magnetic particles of iron oxides on the processes of the oil displacement when the formation is heated by electromagnetic radiation. In articles [18, 23 and 27], a significant increase in the output is reported when using electromagnetic radiation of the 10^6 Hz frequency range. Moreover, the injection of magnetic iron particles allows cracking and oil in the reservoir in the presence of water [23, 27], achieving a decrease in viscosity and an increase in the proportion of light oil fractions in the reservoir. The study of the mechanism of exposure to electromagnetic radiation [23, 27] showed that the electromagnetic field selectively heats iron oxide particles, causing catalytic cracking of oil.

3. Conclusions

The injection of magnetic particles of iron allows cracking and oil in the reservoir in the presence of water, achieving a reduction in viscosity and increasing the proportion of light oil fractions in the reservoir. The destruction of aggregates of magnetic colloidal particles of iron oxides and a multiple increase in the number of the above single colloidal particles as a result of electromagnetic action is accompanied by: an increase in the rate of water injection into the reservoir and the oil recovery factor; a decrease in the rate of growth of deposits of paraffins and salts; an acceleration of oil and water separation; an improvement in the quality of cement stone; an increase in the pH of the medium (alkalization) and, as a consequence, a decrease in the rate of corrosion.

Intensive studies of the use of metal oxide nanoparticles for the intensification of heavy oil recovery processes, which are conducted by research groups in Canada and the United States and other countries, show the prospects for the use of nanoparticles and electromagnetic fields in the oil field development.

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