NANOPHENOMENA AND NANOTECHNOLOGIES IN OIL AND GAS RECOVERY

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Summary

Researches revealed the necessity of taking into account special features of movement of nanoscale objects and processes in oil and gas stratums. Disregard of nanoscale properties of oil and gas stratums qualitatively changes parameters of corresponding technologies and does not allow us to perform highly efficient oil and gas recovery. Nanotechnologies in oil and gas recovery imply use of nanomaterials and management of nanoprocesses in oil and gas reservoirs, oil-field fluids and equipment. Their application will allow us to increase the oil recovery factor from the present 0.3-0.4 (at the average for different types of oil-fields) up to fantastic 0.6-0.65, lowering power inputs 1.5-2-fold, providing profitable oil and gas recovery all over the world for many tens of years.

1. Introduction

Oil has entered into our life so deep that cost of a barrel of oil is announced daily alongside with common weather forecast. And it is clear – power engineering and petrochemistry became the basis of well-being of many countries and their citizens. The forecast of crude reserves as potential energy carriers and raw materials for petrochemistry (Table 1) predetermines the state policy and military strategy in a series of world regions.

#	Countries	Proved reserves, bn. t	Share in world oil resources, %	Annual oil extraction, mln. t	Crude reserves, years	Average well production rate, t/day
1	Saudi Arabia	36.2	19.7	445	81	782
2	Canada	24.5	13.3	129	190	5.7
3	Iran	18.7	10.2	195	96	474
4	Iraq	15.7	8.5	118	133	192
5	Kuwait	13.9	7.6	116	120	402
6	UAE	13.4	7.3	131	102	247
7	Venezuela	11.0	6.0	118	93	21
8	Russia	8.2	4.5	488	17	13
9	Libya	5.9	3.2	86	69	153
10	Nigeria	5.0	2.7	97	52	105
11	Kazakhstan	4.1	2.2	69	59	188
12	USA	3.0	1.6	245	12	1.3
13	China	2.2	1.2	190	12	7.3
14	Mexico	1.4	0.5	140	10	13.9
15	Norway	0.9	0.8	107	8	368
TOTAL (for 15 countries)		164	73.2	2673	61	9.4
TOTAL (all the world)		184	100.0	3652	50	11.5

Table 1. Characteristics of oil-producing regions all over the world for 01.01.2009

Therefore, the world society is interested in good prospects of oil extraction. However, these prospects depend significantly on amount of financial investments into fundamental researches of properties of oil reservoirs and oil-field fluids, into creation of new efficient technologies and elements of oil-field equipment. There is much information about special features of processes of reservoir drive, but conventional understanding of a role of fundamental research in these processes has been not developed yet. It is enough to mention that the basic equations of processes of oil displacement from oil stratums are traditionally grounded on foundations of continuum mechanics, in which so-called "boundary phenomena" (which indeed are nanoscale phenomena) are considered as negligible. These equations work well in pipe hydraulics, in high-size filters and rectifying columns, in high-permeability stratums. As to low-permeability oil-saturated porous mediums, during the last years it is became more and more clear that high recovery factor can be achieved only when decreasing capillary forces keeping oil in rock pores. Here, fundamental knowledge in the area of physics-chemistry and nanomineralogy, and ability to use this knowledge for recovery factor calculation are required. Why «nano»-mineralogy? Because structural elements of surface of pores have nanoscale characteristic dimensions. We have solid grounds to use the cult prefix "nano" here. Textbooks on physics of oil and gas stratums considered physical-chemical problems of oil recovery from the point of view of physics, for example, they mentioned influence of capillary forces. But, at the same time, formulas and schemes for calculation of a recovery factor implied use of continuum mechanics instead of physics and chemistry.

In general, problems leading to a low recovery factor were mentioned (alongside with problems of insufficient oil resources), but correlation of nanoscale effects with macro-dimensional volumes of oil was not taken into account. But after all, this situation is similar to samples from classical mathematics, when one small parameter significantly influences not only a solution of a certain equation, but also its principle features.

General modern interest to oil is based on research of macroeconomists (N. D. Kondratyev) in the area of technological foundations of economic crises. First of all, people create a science connected with new scientific prospects; this period lasts 10-15 years. After that, the stage of development of prototypes takes place – during the next 10-15 years. At last, the third stage - penetration of new technologies into real economy - takes the same time. In the Figure 1, dynamics of innovations in different technological areas (according to Kondratyev's cycles of economic activity) is represented.

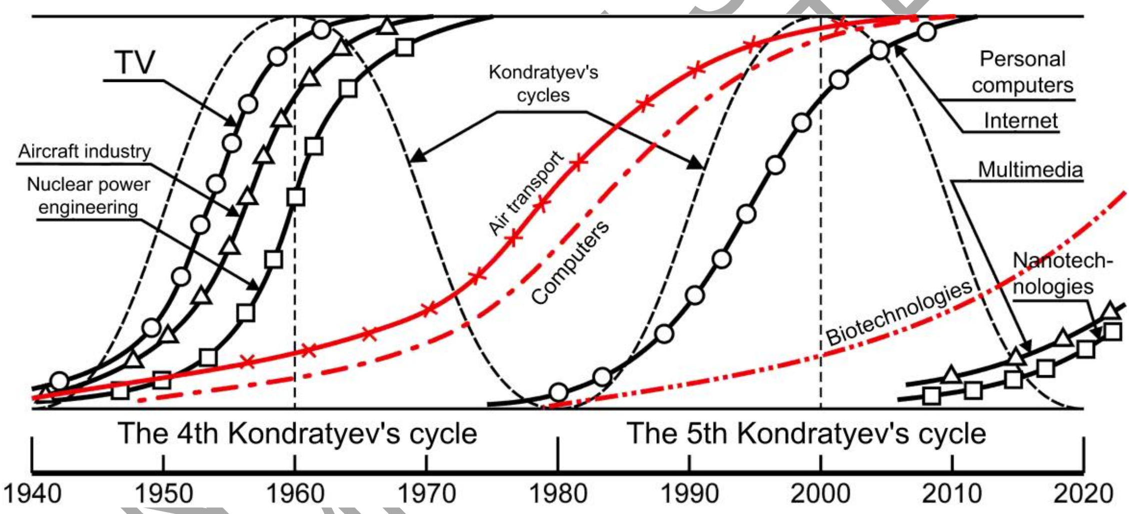

Figure 1. Dynamics of innovations in different technological areas according to Kondratyev's cycles of economic activity

It is evident from Figure 1 that the 4^{th} Kondratyev's cycle (IV technological stage) took place in 1940-1980, when technological progress of economy was provided by development of heavy equipment industry and great chemistry, mass production of cars and airplanes. During the 4^{th} Kondratyev's cycle, nuclear industry and computers appeared.

The 5^{th} Kondratyev's cycle (V technological stage) concerns 1980-2020, when technological progress of economy is provided by development of personal computers and Internet, mass civil air transport, biotechnologies, chemistry of small volumes.

The 6^{th} Kondratyev's cycle (VI technological stage) is expected since 2020, and corresponding technological progress of economy will be provided by development of robotics, biotechnologies, nanotechnologies, management of health of a human due to new medicine, new nature management.

In all these cycles, oil (more exactly, products of its processing - fuel and new materials) have defining value.

Nanotechnologies for new nature management (and, first of all, innovative nanotechnologies in the area of oil and gas recovery) will allow us to solve corresponding problems of the world economy.

2. Oil Production Engineering as a Section of Nanoscience

Application of nanomaterials and nanoparticles as well as management of nanoscale processes in oil and gas stratums is very important for increase of efficiency of oil and gas recovery. It is evident that application of nanomaterials and nanoparticles for increase of efficiency of oil and gas recovery is a nanotechnology, and its scientific substantiation is a subject of nanoscience. In the theory of oil-fields development, mathematical modeling is one of the major methods of research. The purpose of modeling is prognostication of parameters of a certain oil-field development on the basis of mathematical equations describing this process. At such modeling, the purpose can be dual: a) quantitative prognostication of parameters of development, and b) mathematical description of processes taking place in a stratum at oil recovery, for their deeper understanding, management and optimization. Of course, quantitative prognostication is based on mathematical description of processes. In the basis of hydrodynamic description of two-phase filtration (for example, of oil and water), there is the generalized Darcy law connecting speed of filtration of the phase U with pressure difference ΔP, viscosity μ, permeability of a porous medium k and length of a zone of filtration L:

$$U = \frac{k}{\mu}\frac{\Delta P}{L}. \qquad (1)$$

Generalization of the Darcy law for the case of two-phase filtration in the Backley-Leverett model is based on an assumption that permeability of each fluid (phase) depends on its properties and implies introduction of phase permeability (indexing of permeability), phase pressure and viscosity of fluids (since pressure and viscosity of different phases are different) as follows:

$$U_i = \frac{k_i}{\mu_i}\frac{\Delta P_i}{L}. \qquad (2)$$

According to the Buckley-Leverett hypothesis, at water-oil displacement, phase permeabilities k_1 (water) and k_2 (oil) depend only on saturation S, i.e., on volume of the porous space occupied by one of phases (for example, by water). Eq. (2) is based on an assumption that each of the phases moves through “own” system of pore channels and interacts with the other phase only as with a solid skeleton.

Applicability of the generalized Darcy law (2) to the processes of mutual displacement of immiscible fluids is restricted by a zone of relatively slow change of saturation. Difference of pressure of phases P_1 (water) and P_2 (oil) is connected with action of capillary forces. In the case of relatively slow processes of displacement, it was supposed that the difference of pressure of phases is equal to static capillary pressure Pc depending as well as phase permeability only from saturation S. In fact, in this case, the capillary effect in pores is neglected and taken into account only in phase permeability. At the same time, the role of well spacing and difference in values of oil recovery factor (ORF) in the process of displacement of the same oil by water of different composition with the large range of speed of movement of the water-oil interface were not explained. For example, the difference of values of ORF according to results of a great number of laboratory experiments can reach 0.10-0.15. The dependence of phase permeability on permeability of a collector and spacing is difficult to assess. At the same time, application of the same phase permeability for oil stratums with different permeability and for oil-fields with various spacing means neglecting influence of spacing on ORF in the course of hydrodynamic calculations. The divergence between experience of oil-field development and principles of conventional hydrodynamic calculation programs (software packages) was obvious.

Difference between results of calculations of technological parameters of oil recovery and their real values is explained by insufficiently deep understanding of physical and chemical foundations of a process of multiphase filtration rather than by low accuracy of numerical methods and low reliability of values of some geological-technological parameters of the extraction system. On the basis of study of influence of physical-chemical phenomena in stratum systems “oil-gas-water-rock” on processes of hydrocarbons displacement from productive stratums, it is possible to draw a conclusion that without study and consideration of nanoscale phenomena in processes of extraction of hydrocarbons from oil and gas stratums it is impossible to provide growth of efficiency of petroleum industry.

In 1982, the first hydrodynamic calculations concerning the process of differently mineralized water-oil displacement taking into account behavior of clay and capillary-gravitational segregation with capillary hysteresis have been performed. In 1996, specialists advanced a hypothesis according to which water-oil displacement from any productive layers is a physical and chemical process similar to pumping of surface-active agents or solutions of polymers, since the influence of ion exchange of clay minerals with pumped water and influence of microstructure of the porous medium through capillary hysteresis are equally important in the system “oil-gas-water-rock”.

Because of difference of ion exchange activity of different types of clay minerals, in addition to a conventional coefficient of bulk shale of a rock-collector, it was suggested to use a coefficient of active shaliness characterizing physical and chemical activity of clay cement of certain composition in relation to pumped water, and the coefficient of hydrodynamic dispersion of rocks has been suggested for taking into account microstructure of porous environment. Further research demonstrated that they are the major characteristics of porous mediums.

For the last decade, there were many publications about a role of nanoscale phenomena in different areas of science. Specialists in the field of physics and chemistry consider such very important oil and gas technologies as control of wettability, interphase mass exchange and states of superdispersed systems (clay, fluid films on surfaces, micellar solutions) from the point of view of nanoscience and nanotechnologies. Atypical properties of fluids, for example, sharp increase of viscosity on walls of nanocapillary, change of thermodynamic properties of fluids, are manifested on nanoscale. Here, atypical chemical activity at the rock-fluid interface takes place as well. An electrolyte solution (for example, a solution of salt water) in nanopores may serve as an example: at the interface of phases, there are surface charges and electrified surfaces with characteristic distribution of charge known as a double electrical layer. In nanoscale pores, the thickness of the mentioned double layer can overlap completely the lateral dimension of pores that leads to a significant change of structure of a liquid, and, hence, to change of a process of its motion in nanostructures.

According to recommendations of the 7th International Conference on Nanotechnologies (Wiesbaden, 2004), the following types of nanomaterials exist: nanoporous structures; nanoparticles; nanotubes and nanowires; nanodispersions (colloids); nanostructured surfaces and films; nanocrystals and nanoclusters. Besides small-size particles, nanoparticles include surface nanostructures (fillets, ledges, grooves, walls), volume nanostructures (pores and capillaries), films of mediums with nanoscale thickness, which are of crucial importance in processes of oil displacement in porous rocks.

In a volume phase, properties of mediums and materials organized by structural elements with nanoscale dimensions are not determined unequivocally. Changes of characteristics are caused not only by decrease of dimensions of structural elements, but also by manifestation of quantum mechanical effects, wave nature of transfer processes and by a dominating role of an interface. Nanoparticles are both too small (for direct observation and study) and too great (for quantum mechanical calculations). At the same time, the main priority is creation and optimization of nanotechnologies. Therefore, at modeling of nanotechnologies, it is recommended to consider nanoparticles as structural components (elements) of larger dimensions - macro- and meso-dimensions. Originally, nanoscale objects are determined as objects with at least one dimension within a range of 1-100 nm. The special feature of nanoobjects is in a fact that such dimensions are comparable with the radius of action of interfacial interaction forces, i.e., with a distance where interaction of objects at atomic level in ordinary materials must be taken into account.

In 1991, carbon nanotubes with a diameter of 0.5-1.0 nm were obtained, and the term nanosystems begun comprise the structures surrounded by a gas or liquid medium, which characteristic dimension being within 0.1-100 nm. These are intermediate structures between atoms and macroscopic physical bodies. For this reason, ultrafine systems including clay, aerosols, micellar colloidal solutions (muds), polymeric sols and gels, surface fluid films, are subjects of nanoscience. In this case, characteristic radiuses of ions lie within the range of 0.1-1 nm and regulate properties of clay minerals with dimensions of 20-40 nm.

Analysis of nanoscale phenomena at the interface of phases in porous mediums has led scientists to a conclusion about a defining role of capillary hysteresis. The magnitude of capillary hysteresis depends on wetting properties of rock surface defined by charge interactions. Both in hydrophilic and hydrophobic medium, capillary hysteresis is directed against movement of displaced oil. Neglecting capillary hysteresis leads to significant errors when designing the process of oil-field development. The multiphase filtration in the porous medium can be carried out either by means of motion of each of phases through own systems of pore channels or by means of motion of the displaced phase in macrodisperse parts. Analysis of physical and chemical literature showed in the case of water and oil contact, dispersion of the latter takes place. Taking into account this fact, specialists have formulated the law of oil displacement in porous rocks stating that at displacement of oil from an oil-field stratum by water solution pumping, oil is dispersed into separate parts (aggregates, ganglia, blobs, bypassed oil, clusters – macrodisperse parts), distribution of which by sizes is determined by capillary hysteresis in the system «oil-water-rock». Actually, this discovery has underlined importance of nanoscale phenomena of wetting in the macroprocess of oil displacement.

The law of filtration, taking into account different sizes of clusters of oil (through introduction of the index R of the length of a cluster of oil l_R), can be represented as follows:

$$U_i = \frac{k_i}{\mu_i} \frac{\Delta P_i}{l_R} \quad . \tag{3}$$

We must notice that all parameters in formulas (1) and (2) are indexed. The specified approach based on the corresponding discovery has allowed us to perform calculations that demonstrated a good fit to real oil-field statistics. At the beginning of research of ion-exchange phenomena (1970s), their significance for efficient oil displacement has been proved without underlining characteristic scale of these phenomena. Taking into account an opinion of physicist and chemists, it is necessary to recognize that many technologies managing oil displacement from porous mediums (i.e., technologies purposefully managing nanophenomena) are nanotechnologies in oil and gas recovery.

In 2006, as a result of analysis, it has been demonstrated that oil-driving (extraction) nanotechnologies include thermal, physical, and biological technologies, and chemical and gas technologies occupy an intermediate position between nanotechnologies and macrotechnologies depending on applied reagents and the mechanism of their influence on a system “oil-gas-water-rock”. Certain discomfort connected with the use of the term “nanotechnologies in the area of oil and gas recovery” in some specialists is caused by their unwillingness to understand that this term means “technologies of use of nanomaterials and management of nanoscale processes (including wetting and ion-exchange) for the purpose of increase of efficiency of oil and gas recovery”.

Petroleum science (the main purpose of which is rational development of hydrocarbon resources) being a part of Earth sciences and accumulating such scientific disciplines as geology, mathematics, physics, chemistry, has own specific subject of study - physical and chemical nanoprocesses in rocks, oil-field fluids and equipment including both nanophenomena and methods of their accounting in geological-hydrodynamic and technical-economic calculations for exploitation of oil and gas resources. Here, an analysis of oil and gas fields with nanoscale hydrocarbon collecting pores (with the characteristic size of pores up to 100 nm) plays a significant role in increase of the resource basis of oil recovery. Oil and gas extraction from such oil fields requires application of specific technological solutions.

The Nobel Prize winner R. Smalley believed that the main problem faced by the world community or even by humankind as a whole is the problem of energy supply. According to his research, the level of power consumption will double (at least) to the middle of the 21st century, so it is necessary to master new technological processes to increase power generation, and the problem of power supply of humankind can be solved only by those directions of the modern science, where scientists can manage matter and processes at an atomic level. Exactly, these directions are consolidated in nanoscience.

Taking into account physical-chemical nanophenomena in oil and gas stratums in corresponding hydrodynamic models allows us to develop adequate scientific foundations of oil and gas nanotechnologies (of the oil and gas branch of nanoscience) that will allow us to create a uniform methodological basis for modeling of corresponding processes of oil and gas fields development for the purpose of perfection of technologies of oil and gas recovery.

Of course, physical (and more exactly, physical-chemical) knowledge concerning specific processes in oil and gas stratums has been strongly changed for the last 25 years. In fact, this new understanding of this matter became the factor using which it is possible to improve significantly the efficiency of the whole gas-and-oil producing industry both in respect of oil recovery increase and power consumption decrease. Investments to nanotechnologies of oil and gas recovery will bring maximum financial profit in the shortest time period in comparison with investments into other fields. So, for example, special treatment of well bottom zones is repaid in a half a year, increase of ORF of developed oil-fields will allow us to satisfy oil demand. Creation of the gas-hydrate branch of the petroleum industry will also bring sufficient profit, since it will allow us to transport gas in the form of gas-hydrates, utilizing associated and low-pressure gas; it will create thousands of vacancies in this sphere, lead to diversification of transportation of tank gas and pipe-less gasification of rural places. Current results of research in this matter already prove necessity of active fundamental study of nanophenomena of oil and gas recovery and transportation, and also optimization of their further processing.

Even U. Hartmann, a famous specialist in the area of nanotechnologies mentions the area of application in oil and gas recovery. According to his opinion, today's annual oil demand is equal to 3.4 billion t/year, and accurately enough explored reserves (taking into account standard technologies of extraction) are about 140 billion ton. According to his estimate, about 100 billion ton of hydrocarbon resources can exist in oil fields of the Arctic zone and at the bottom of the sea. However, modern technologies, especially for northern areas, where oil is high-viscous, are required. Thus, oil-and-gas nanotechnologies are those technologies, which, due to use of nanomaterials and management of nanoprocesses, allow us to increase power efficiency and decreasing expenditures in oil and gas production industry, and their scientific substantiation represents a separate branch of nanoscience.

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Biographical Sketch

Khavkin Alexander Yakovlevich was born in 1953 in Moscow. In 1975, he has graduated from the Moscow Institute of Petrochemical and Gas Industry (MINKHiGP) (currently - Gubkin Russian State University of Oil and Gas). In 1983, he has presented a Ph.D. thesis at the Institute of Geology and Fossil Fuel Development (IGiRGI). In 1996, he has defended the thesis for the Doctor's degree "Hydrodynamic foundations of development of oil pool with low-permeable collectors" at the Krylov All-Russian Oil and Gas Scientific Research Institute, specializing in "Development and maintenance of oil and gas fields", and has been awarded with a diploma of the Doctor of Technical Sciences.

He worked in the IGiRGI (1975-1979), VNIIneft (1979-2001). In VNIIneft, he has been elected a General Technologist on development of oil-fields with low-permeable and clay-containing collectors (1991) and appointed a Director of the Scientific Center for Technologies of Development of Hard-Recovering Oil Resources (1997). Since 2001, he is the Chief Scientist at the Institute of Problems of Oil and Gas of the Russian Academy of Sciences (Moscow).

In 1997-2009, he was a professor in the Gubkin Russian State University of Oil and Gas. Since 2009, he is a professor of the Udmurt State University, the Scientific Supervisor at the Scientific and Educational Center «Nanotechnologies for the Fuel and Energy Complex» of the Izhevsk State Technical University.

He is the Honorable Oil Industry Worker of the Russian Federation, a full member of the Russian Academy of Natural Sciences, the European Academy of Natural Sciences, the New York Academy of Sciences. His specialization is oil and gas hydrodynamics in relation to geological features of strata, technologies of increasing ORF and GRR, intensification of development of oil and gas fields, physics and chemistry of oil and gas strata, energy saving, economic criteria, management of the state of GHs, nanotechnologies.

He is the author of the scientific discovery «Laws of oil displacement in porous mediums» (1989) revealing the role of nanophenomena of wetting in processes of oil displacement, new directions (in the area of oil and gas recovery) in nanoscience. He is also the author of more than 400 publications (including 11 monographs and more than 45 patents of the Russian Federation). He is a member of the scientific board of the Editorial Board of the journal «NANOtechnologies. Ecology. Manufacturing», the laureate of four awards.

He is a member of the Program Committee of the Eurosymposium on ORF of the EAGE (since 2002), the organizer of the international conferences «Nanophenomena at Development of Hydrocarbon Fields: From Nanomineralogy and Nanochemistry to Nanotechnologies»: NANOTECHOILGAS-2008 and NANOTECHOILGAS-2010, a participant of international symposia in Australia, Brazil, Hungary, Denmark, Egypt, Spain, China, Norway, Russia, France, Japan.