The mineral fuel is concentrated in the earth’s crust as accumulation of carbon (different coals and schist) and hydrocarbon (oil and gas deposits). For a long time the scientists believed that hydrocarbon accumulation with molecular weight more than 60 exists in the earth’s crust in liquid form and lighter ones in gaseous state [1]. It often happens that the researchers become interested in some process or phenomenon just by accident and then they go deeply into the matter if it is up to date and necessary. The same happened with gas hydrates. The natural gas hydrates existed for ever and influenced greatly on formation and preservation of planetary material, but they were discovered by accident [11].

Nowadays gas hydrates are considered to be one of the most promising unconventional sources of hydrocarbons and energy in the twenty first century [3]. But what is the history of discovery, what happened before and what takes place nowadays. We will tell you about that and other things in our material.

For the first time gas hydrates were derived in laboratory environment but the exact name of the author is unknown [14]. Yuriy A. Diadin and his colleagues [4, 10], as well as Yuriy Makogon [9], believe that Joseph Priestley was the first who observed gas hydrate (sulfur dioxide hydrate) in 1777–1778. But as Sloan indicated [16], the temperature in experiments of J. Priestley was equal to 17 °F (−8.3 °C), and it is impossible to tell for sure that crystallization of solid phase that was observed during cooling 

The literature sources dealing with the history of gas hydrate studies and discovery of possible existence of gas hydrate deposits in natural conditions were analyzed. They contain facts proving that within 1966 and 1969 the conditions for formation of hydrates in porous medium were researched at the Department of Gas and Gas Condensate Deposits Development and Exploitation of Gubkin Russian State University of Oil and Gas. The first experiments were set up by the Ukraine-born Yuriy F. Makogon, Department Assistant Professor. The results proved possibility of formation and stable existence of gas hydrates in earth’s crust and became a scientific substantiation of natural gas hydrate deposits discovery. In 1969 the exploitation of Messoyakha deposits in Siberia started and it was the first time when the natural gas was derived directly from hydrates. The same year that invention was officially recognized and registered. Following the comprehensive international expert examination the State Committee on Inventions and Findings of the USSR Council of Ministers assumed that the citizens of the USSR Yuriy F. Makogon, Andrej A. Trofimuk, Nikolaj V. Cherskij and Viktor G. Vasilev made a discovery described as follows: “Experiments proved previously unknown ability of natural gas to form deposits in the earth’s crust in solid gas hydrate state under definite thermodynamic conditions (Request dated March 19, 1969)” The authors were presented with diplomas on March 4, 1971.

From then onwards the issue of natural gas hydrates existence was widely researched all around the world. In 1985 Yuriy F. Makogon became a Professor. Since 1973 he was a head of the gas hydrate laboratory in the All-Russian Scientific Research Institute of Natural Gases and Gas Technologies. Within 1974–1987 he was a head of the gas hydrate laboratory in Oil and Gas Research Institute RAS. In 1992 he was invited by one of the largest universities of the USA to arrange modern laboratory for gas hydrate study. The laboratory was created in the Texas University, USA and in 1995 Yuriy Makogon became its head. As far as interest in gas hydrates increases Yuriy F. Makogon reports at 27 international congresses and conferences, gives lectures in 45 world leading universities, functions as an academic adviser and participates in different international programs on research and exploitation of gas hydrate deposits in USA, Japan and India. The heritage of the scientist includes 27 patents, eight monographs (four of them were translated and published in the USA and Canada) and more than 270 scientific articles.

Key words: Yu. F. Makogon, natural gas, hydrates, deposits, discovery.

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The mineral fuel is concentrated in the earth’s crust as accumulation of carbon (different coals and schist) and hydrocarbon (oil and gas deposits). For a long time the scientists believed that hydrocarbon accumulation with molecular weight more than 60 exists in the earth’s crust in liquid form and lighter ones in gaseous state [1]. It often happens that the researchers become interested in some process or phenomenon just by accident and then they go deeply into the matter if it is up to date and necessary. The same happened with gas hydrates. The natural gas hydrates existed for ever and influenced greatly on formation and preservation of planetary material, but they were discovered by accident [11].

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Mineral resources of Ukraine

P. Makogon

In 1810 [13] that chlorine (at that time chlorine was called murium oxide) water crystallizes faster (i.e., under higher temperature) than clear water, but dry chlorine gas does not crystallize even under -40 °F (-40 °C). That is how chlorine hydrate was discovered and in 1823 Michael Faraday determined its composition.

During the next century the scientists worked a lot on classification of molecules of different substances being able to form clathrate compounds; the conditions necessary for steady state of each substance were experimentally investigated. But as far as people did not know about existence of hydrates in natural environment at that time, this subject matter remained just for academic interest [11].

On the cusp of the 19th and 20th centuries the hydrates of different substances, including methane, ethane, propane and other natural gas components, were discovered; the possibility of existence of double hydrates—structures containing molecules of two hydrate-forming substances—was also discovered. In 1829 Löwig discovered bromine hydrate, in 1840 Wöhler discovered hydrogen sulfide hydrate and in 1888 Paul Villard obtained hydrates of methane, ethane, ethylene, acetylene and nitrogen oxide [1].

Besides, the direct and semiempirical methods for estimated analysis of hydrates were offered. In total till the first half of the 20th century the researches focused more on detection of substances being able to form hydrates and of temperature and pressure conditions necessary for their formation. Later on the process of natural gas extraction, processing and transportation took place under high pressure and with high flow rate. Under such conditions the Joule-Thompson effect was observed at some sections of pipelines and processing facilities when the temperature of gas flow decreased rapidly and if there was water phase in the flow the gas hydrate was formed and influenced the efficiency of processing facilities, blocked the pipelines.

So in the middle of 1930s the second phase of gas hydrate investigation started when E. G. Hammershmidt [15] demonstrated that gas hydrates cause formation of slugs in gas pipelines under the temperature above 0 °C, which result in major complications and accidents at processing facilities. In 1934 Hammershmidt published the results of examination of pipelines in the USA where in winter they suffered from formation of slugs. It was believed that condensate water creates ice slugs. Based on laboratory experiments Hammershmidt demonstrated that solid slugs consist not of ice but of hydrate of transported gas. The interest in gas hydrates increased greatly [7].

Hammershmidt’s researches initiated investigation of industrial formation of hydrates and methods for their prevention in oil and gas extraction and transportation systems. Even today industrial formation of hydrates is still one of the major problems of the gas industry and huge resources are used for its solution [5, 17].

The paper of academician Nikitin (1936) was an important stage in the history of gas hydrates study. He demonstrated that gas hydrates are clathrate compounds where gas molecules are trapped in separate cages formed by water molecules due to hydrogen bond.

Thereafter a small group of researchers headed by Dr. D. Sloan in Colorado School of Mines investigated physics of different clathrates and developed the first predictive models of their formation. The main purpose of this work was (and remains) development of different methods preventing hydrate formation, as well as searching for chemical additives inhibiting hydrate formation process [1]. So we may say that gas hydrates studies were applied in practice for development of principles for prevention and control of their formation. In return it required detailed study of gas hydrates properties, their structure, thermodynamic stability zones and kinetics of their formation and dissolution.

The next stage of gas hydrates study was in 1940s and it was related to discovery of natural gas hydrates that had a dominant role in formation of planets, atmosphere and hydrosphere of the Earth but were unknown [7].

First of all, two clathrate structures of crystals: “I” and “II” (1949–1954) were discovered based on X-ray crystallography; and after almost 45 years (1994) structure “I” was discovered [6]. So far more than ten structures of gas hydrates existing under different pressures and temperatures were discovered. Most of new structures were discovered by the team of scientists from the Institute of Inorganic Chemistry, Siberian Branch of RAS.

Second, a hypothesis was suggested that there are gas hydrate deposits in permafrost zone.

The first assumption on existence of gas hydrate deposits in permafrost zone of Canada was made by Professor Donald L. Katz, Michigan University, in 1943 but they failed to prove their existence by well drilling. Next time theoretical papers of Ivan N. Strizhov (1946), M. F. Mokhnatkin (1947), Nikolay V. Cher- skiy, as well as experimental researches of Yurii F. Makogon (1945–1946) demonstrated possible existence of gas hydrate deposits in natural environment [14].

Experimental researches were very important as far as existence of gas hydrate accumulations in cooled layers was doubted by scientific community. It was necessary to prove possibility of formation of hydrates in natural porous medium and of formation of gas hydrate deposits. The first experimental research of conditions for formation of natural gas hydrates in porous medium was conducted by Yurii F. Makogon, Department Assistant Professor, at the Department of Gas and Gas Condensate Deposits Development and Exploitation of Gubkin Russian State University of Oil and Gas and published in Gas Industry Magazine. The results proved possibility of formation of gas hydrates in porous medium, in real drill samples, and became a substantiation of existence of gas hydrate deposits in earth’s crust. The results of experimental study of hydrates formation and dissolution in real drill samples were reported by Yurii F. Makogon at the scientific conference of young oil-well experts in Moscow in April 1965 and were awarded with the first prize [6].

Four years later, following the comprehensive international expert examination and conclusion of the RAS General Committee the State Committee on Inventions and Findings of the USSR Council of Ministers, according to the Regulation on Findings and Inventions, assumed that the citizens of the USSR Yurii F. Makogon, Foma A. Trebin, Andrey A. Trofimuk, Nikolay V. Cherskiy and Viktor G. Vasilyev made a discovery described as follows: “Experiments proved previously unknown ability of natural gas to form deposits in the earth’s crust in solid gas hydrate state under definite thermodynamic conditions (March 24, 1969)”. The authors were presented with diplomas on March 4, 1971.

At the same time on December 24, 1969 the exploitation of Messoyakha gas hydrate deposits in the Polar Regions started. The author’s report on laboratory and industrial results made at the 11th International Gas Congress in June 1970 had international resonance. Later on the national programs for investigation and exploitation of hydrate deposits were initiated in many countries.

When we analyze history of this worldwide important discovery we cannot just skip personal history of the scientist and researcher who made this world known discovery possible.
Yuriy F. Makohon was born on May 15, 1930 in village Vesle, Velykooleksandrivskyi District, Kherson Oblast. In 1951 he graduated with honors from Krasnodar Oil Technical School and entered Gubkin Moscow Institute of Oil, Gas and Oil Industry Department.

The scientific career of gas engineer Yuriy F. Makogon started at unique recently discovered Shebelinka gas field in Ukraine where he was employed as gas production operator in 1956. In 1957 Yuriy Makogon was promoted to the main foreman in the field and later to the Deputy Chief Engineer.

Formation of gas hydrates in wells and industrial gas pipelines was the most complicated problem young expert faced with. The experience of Yuriy Makogon in fighting against industrial hydrates obtained in Shebelinka gas field and their study in laboratory while working on his first dissertation, as well as analysis of abnormal conditions of existence of hydrocarbon deposits in cryolithic zone after discovery of anomalous frozen rock mass in Eastern Siberia contributed to discovery of existence of natural gas hydrates. Usually important scientific discoveries are made at the intersection of two problems. PhD thesis “Gas Hydrates, Formations and Their Prevention during Gas Extraction and Transportation” was the result of such studies and it was the first significant scientific paper on natural gas hydrates defended by the scientist in 1963.

Meanwhile Markhinskaya well 1 850 m deep drilled in USSR in the north-west of Yakutia opened anomalous frozen rock mass, about 1 150 m, it is almost twice more than any known before. Thermogradient within the range of frozen rocks did not exceed 0.5°C/100 m, and it was equal to 1°C/100 m in the subpermafrost layer of the open cut and it corresponds to gas hydrate existence conditions. It was necessary to prove it. As a result gas hydrate deposits were discovered.

Yuriy Makogon describes these events in his paper in detail [7]. In 1964 Yuriy Makogon and Kaplan S. Basniev, PhD student at the Department of Gas Deposits Development and Exploitation of Gubkin University of Oil and Gas, were sent on a business trip from Moscow to Yakutia. The purpose of the business trip was to sign an Agreement on Cooperation in the Areas of Science and Technology between Yakutia Affiliated Branch of Siberian Branch of the USSR Academy of Science, Yakutia Regional Geological Department (YaRGD) and the Department on the issue of fighting against formation of hydrates in gas wells and gas pipelines in conditions of Yakutia. Young scientists were hosted by Nikolay V. Cherskiy, the Chairman of the Presidium of Yakutia Affiliated Branch of Siberian Branch of the USSR Academy of Science, Doctor of technical sciences, and later Associate Member of the Academy of Science (1968) and the Academician of the Academy of Science of USSR (1981). Yuriy Makogon met Nikolay Cherskiy before in Moscow in 1962 when Makogon had a PhD completion seminar at the Department. Cherskiy was satisfied with the paper of young scientist. The seminar was successful. The experience of Yuriy Makogon at then the largest Shebelinka gas condensate field in Ukraine came in handy during conversation. That was also when Cherskiy invited Makohon to come to Irkutsk. It was time when gas hydrate fields were developed there and they needed experts in the issue of hydrates formation during transportation of gas in severe environment of Yakutia.

After visiting Yakutia they started works on fulfillment of the signed agreement in Moscow. The lead specialists of the Department B. B. Lapuk and E. A. Bondarev, thermodynamics experts and leading mathematicians, participated in this work. Yuriy Makohon conducted experiments studying conditions for formation and dissolution of gas hydrates in wells and gas pipelines. PhD students K. S. Basniev, S. N. Zakirov, B. E. Somov and A. A. Bubnov and D. P. Sidorov from YaRGD took an active part in experiments.

The previous great scientific work, work on PhD thesis, received research materials and experience obtained by Yuriy Makohon in the field initiated idea about existence of gas hydrate deposits. The first article where Makogon described his idea about existence of gas hydrate deposits in permafrost area was written and sent to Gas Industry Magazine. But the editorial office sent the submission back refusing to publish unproven idea and having added that “Hundreds of wells were drilled in such areas but no one found hydrate layers.” Yuriy Makogon insisted on publication and the article was published in section “Subject for discussion” (Gas Industry. #5. 1965). It was necessary to prove the idea. So Yu. F. Makogon made facilities to create conditions for formation and stable existence of hydrates in porous medium of real rocks. The laboratory experiments demonstrated that gas hydrate deposits may exist. The results of such work were published by Yuriy Makogon in brochure edited by K. S. Basniev (1966).
At the end of August 1965, having become Assistant Professor of the Gas Deposits Exploitation Department Yuriy Makogon leaves for India. There he lectures on gas extraction in Indian School of Mines. It is interesting that right there being far from his motherland he arrives at the idea to submit request on discovery of gas hydrate deposits. Yuriy Makogon remembers that it was after radio program on recording of scientific discoveries he had heard on Mayak radio station [9]. He comes back home, enlists help of his teacher and colleague Nikolay V. Cherskiy, and starts with collecting of materials for recording of his discovery. He received all necessary experimental data already. All he had to do is to go through the procedure. Having come back to Moscow Yu. F. Makogon and N.V. Cherskiy go to the Committee on Inventions and Findings of the USSR Council of Ministers where they meet Yulia P. Konishnaya, an expert of Scientific Discoveries Department. After statement of the heart of the matter it was decided to submit immediately.

But the idea itself and even publication as a basis for request was not enough for positive decision. N.V. Cherskiy made a wise decision to add more authors such as Academician Andrey A. Trofimchuk, Viktor N. Vasiliev, Head of Geological Survey of the Gas Industry Ministry, Professor Foma A. Trebin, Head of the Department of Gas Deposits Development and Exploitation of Gubkin University of Oil and Gas. The composite author was quite respectable: Academician, Associate Member, two Doctors and one Candidate. The request was submitted and registered on March 19, 1969. The request was submitted and registered on March 19, 1969. The request was submitted and registered on March 19, 1969.

In conclusion should be mentioned that today gas hydrate accumulations were discovered by different methods in many parts of the world. The aquatic deposits of methane in hydrate state attract special interest. But there is no industrial process for their development and exploitation. The only thing we have is political statements of different countries and that's it. Nowadays we know only three gas hydrate development methods once offered by Yuriy F. Makogon. So the inventors, researchers and enthusiasts still have a lot of work to do.

This year on May 15 Yuriy Makogon will celebrate his 89th birthday. But he is still ready to help curious and full of energy researchers of the world. The whole generation of young scientists was brought up on his books and scientific publications. The papers and scientific researches of

Authors of discovery № 75.
From left to right: N. V. Cherskiy, A. A. Trofimchuk, Yu. F. Makogon, F. A. Trebin, V. G. Vasiliev

Professor Yu. F. Makogon with colleagues.
Texas National University (USA)
gas hydrate properties conducted by Yuriy Makogon became the basis for creation of tools for search and exploration, estimation of reserves, development and creation of production technology. We can tell for sure that the issue of gas hydrates unites only people with proactive attitude, enquiring mind and will to life.

REFERENCES


BRIEF INFORMATION ABOUT THE AUTHOR OF DISCOVERY

Dr. Makogon is a world-renowned expert on gas hydrates. In 1965-66 he has experimentally proven that gas hydrates may accumulate as large natural deposits in porous layers. Yuri F. Makogon graduated with honors from the Krasnodar Technological School in 1951 and from the Gubkin Petroleum Institute in Moscow in 1956, started his career that year at the Shebelinskoe gas Field, in the Ukraine. In 1962 he received M.S. (Candidate) degree at the Gubkin Oil-Gas Institute, followed by his Dr. Sc. in 1975, and full Professorship in 1985. From 1961 to 1974 he worked at the Gubkin Institute of Oil and Gas. As a professor, he taught at the Indian School of Mines in Dhanbad from 1965 to 1967, and in 1973, at the Freiberg Mining Academy of Germany. He worked as a consultant in many countries. He helped remove multiple hydrate plugs in perma- frost regions and in the offshore conditions. In 1969 this discovery was formally recognized and registered in the USSR. Yuri F. Makogon born May 15, 1930 in Ukraine. Dr. Makogon has authored eight monographs, including six books on gas hydrates and over 270 scientific papers. He holds 27 patents and has close to 60 years of experience in education and research for the oil and gas industry. Yuri F. Makogon is a Full Member of the Russian Academy of Natural Science. He was one of the founding members of the RANS in 1990. He had served as the first Chairman of the Oil and Gas Section of the RANS. He is a Full Member of the Oil and Gas Academy of Ukraine since 2010. Yuri is also a Member of the International Society of Petroleum Engineers. He is the first Chairman of the SPE International, Russian Section in 1991–1993. He is also a member of the editorial board of the International Journal of Geology and Mineral Resources of the World Ocean. He was the International Distinguished SPE Lecturer for 2002–2003. He is presently the USA Section Regional Secretary of the RANS.

During his career Prof. Makogon held a number of leadership positions including head of the Gas Hydrate Laboratory of Petroleum Engineering Department at the Texas A&M University (1995–2010). Chairman of the technology group of international CODATA committee (1997–2008), and Director of the Russian Academy of Science and Institute of Oil and Gas Research hydrate lab and at the Hydrocarbon and Environment Institute of the RANS (1987–1993). From 1974 till 1987 he served as the head of the gas-hydrate laboratory at the Central Gas Research Institute of the USSR. Dr. Makogon joined Texas A&M University in 1992 and has established a new direction in the research of water-gas phase behavior in the Earth’s stratum, discovered a number of important new physical gas hydrates properties, researched kinetics and morphology of hydrate crystals, structural hydrogen bond memory of water, hydrate crystal transformation, and expanded knowledge of the existence of tremendous gas reserves in the hydrate form, proposed hydrate exploration and appraisal methods and technologies for development of hydrate reservoirs. Yuri has retired in 2008. Dr. Y.F. Makogon holds an Honorary Doctorate of the Nikolaev Institute of Inorganic Chemistry Russian Academy of Science since 2005. His awards include Heritage Award recognizing his lifetime scientific accomplishments during the 2016 Offshore Technology Conference in Houston Texas on May 3, 2016; Honorary Medal “Star of Success”; 2015. His awards also include Golden Jubilee Medal of Russia in 1970; the Gubkin State Prize 1989. Honorary Diploma of the Mendeleev Chemistry Society of Russia in 1982; Golden P. Kapt'sa Medal for Scientific Discovery in 1997; Lifetime Achievement Award of Honor by the Sixth International Conference on Gas Hydrates in 2008, Honor Certificate “Most Cited Articles 2007” from the J. Petroleum Science, London 2012; honorary sign “For Merits” in Science and Economics of Russia (2005). The First Prize at the Chess Tournament of Indian School of Mines in 1967; The First Prize at Young Petroleum Scientist Conference of Russia in 1965; Winner of the Ukraine State Inventors Competition in 1958. He has two children and three grandchildren. His hobbies include art painting, traveling and photography [12].

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http://www.amechq.org/programs/award/bio/yuri-f-makogon