HYDRATES OF NATURAL GAS

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Contents

Summary

Gas hydrates are clathrate physical compounds, in which the molecules of gas are occluded in crystalline cells, consisting of water molecules retained by the energy of hydrogen bonds. Gas hydrates can be stable over a wide range of pressures and temperatures. All gases can form hydrates under different pressure and temperature.

The crystalline structure of solid gas hydrate crystals has a strong dependence on gas composition, pressure and temperature. Presently three crystalline structures are known for moderate pressure and nearly ten structures in the pressure range above 100 MPa. For example, methane hydrate can be stable from 20 nPa to 2 GPa at temperatures from 70 to 350 K.

Formation of gas hydrate occurs when water and natural gas are present at low temperature and high pressure. Such conditions often exist in oil and gas wells and pipelines. Hydrate plugs can damage equipment of gas transport system. Petroleum industry spends over two million US$ each day to prevent hydrate formation in wells, pipelines and equipment.

Natural deposits of gas hydrates also exist on Earth in colder regions, such as permafrost or sea bottom areas. Natural gas hydrates are unconventional energy resources. Potential reserve of gas in hydrate deposits is over $1.5x10^{16}$ m^3 distributed offshore and on land. About 97% of natural gas hydrates have been located offshore and only 3% on land. What matters is not the potential resource of hydrated gas, but the

volume of gas that can be commercially produced.

At present time there are several federal research programs in a number of countries for development of gas hydrate deposits. Over 220 gas hydrate deposits were discovered, over a hundred wells drilled, kilometers of cores studied. Gas hydrate resource is distributed conveniently for development by mostly every country.

Special properties of hydrated cores were studied, and effective tools for recovery of gas from hydrate deposits and new technology for development gas hydrate fields were developed. There is a long-term commercial production of natural gas from hydrates in Siberia. Researchers continue to study the properties of natural gas hydrates in reservoir conditions and to develop new technologies for exploration and production of gas from hydrate deposits in different geological conditions.

1. Introduction

The history of humanity is characterized by an ever growing use of energy. The 20th century has been one of high population and energy consumption growth. Over the 20th century, the population on Earth grew four-fold, exceeding 6.3 billion, while the energy consumption grew by over an order of magnitude, from 0.9 billion Tons of Oil Equivalent (TOE) in 1900 to 10.88 billion TOE at the end of 2006.

The rate of modern civilization growth in the future will depend on numerous factors, but the quality and quantity of energy used will be one of the most important factors. The data presented in Figure 1 reflect the distribution and the changes of energy sources in time. Also, it is well known that energy consumption distribution by country is very different (Table 1).

Country	Total Energy Consumption, mln t.o.e	%	Population, mln.	%	t.o.e./capita
World	10879	100.0	6600.0	100.0	1.65
USA	2326	21.4	300.0	4.5	7.75
Russia	705	6.5	142.0	2.1	5.00
S.Korea	226	2.1	48.4	0.7	4.70
Japan	520	4.8	127.4	1.9	4.10
China	1698	15.6	1306.0	20.0	1.30
India	423	3.9	1100.0	16.6	0.38

Table 1. World energy consumption, 10^6 TOE, year 2006.

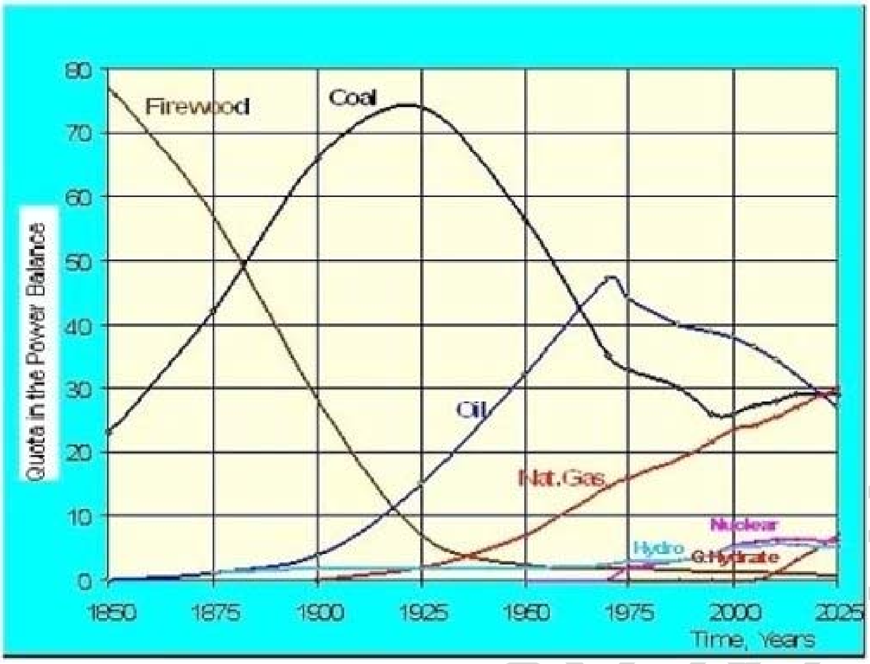

Figure 1. World Energy Balance, percentage of different energy source in time.

All natural gases can form hydrates under different pressure and temperature. Gas hydrates can be stable over a wide range of pressures and temperatures. On the **Figure 2** showed P-T equilibrium for methane-water conditions.

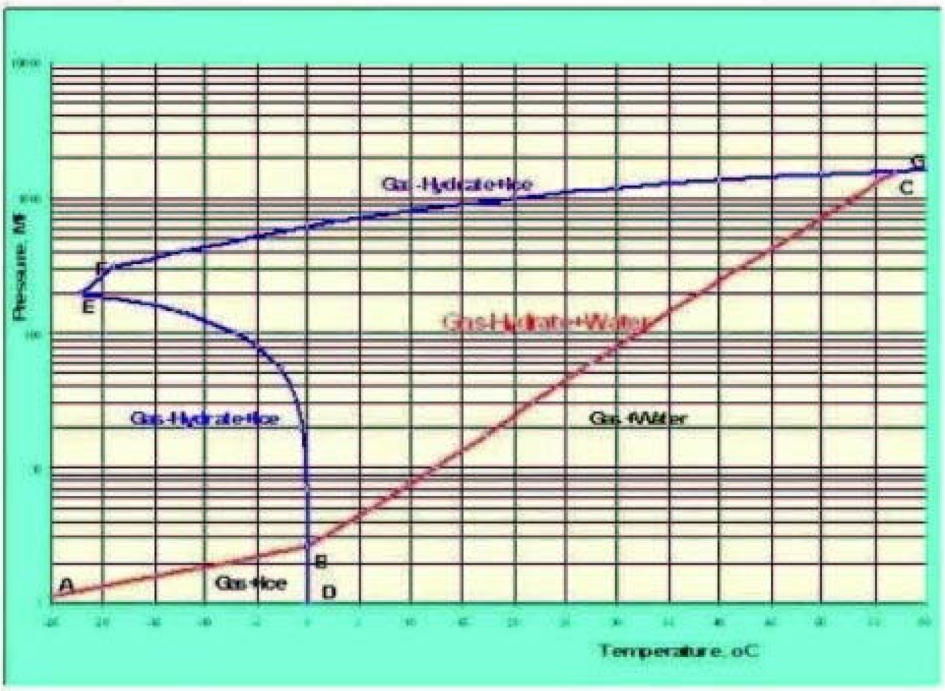

Figure 2. Pressure vs. temperature equilibrium curves for methane-water system at hydrates stability conditions.

Figure 3. Map of Discovered Gas Hydrate Deposits. BSR = deposit located by seismic refraction.

At present time we know that a huge potential resource of hydrated gas exists on our planet and it has been estimated in over $15x10^{12}$ TOE. If we will produce only 15 to 17 % from this resource, it can be a sufficient supply of energy for 200 years. Gas hydrate deposits exist on land in the polar region, and offshore around the globe. Over 220 Gas Hydrate Deposits (GHD) have been found in the world. A map of the discovered GHD is shown in Figure 3. The production of hydrated gas could be used to contribute not only to the sustained economic development of the individual countries, but also to the political stability in the world.

1.1. A Brief History of the Discovery of Natural Gas Hydrates

Gas hydrates were first obtained by Joseph Priestley in 1778 under laboratory conditions by bubbling SO_2 through 0°C water at atmospheric pressure and low room temperature. Priestley was a gifted researcher of his time, who discovered a number of gases, in particular, oxygen, hydrogen, SO_2 and others. However, when describing the crystals he obtained, he did not name them hydrates. About 30 years later, in 1811, similar crystals of aqueous chlorine were named hydrate of gas by Davy. Some scientists consider Davy to be the discoverer of gas hydrates; however, Priestley was the first scientist to create gas hydrates in a laboratory. The results by Davy did not draw the attention of contemporaries and the studies of hydrates did not gain serious development for almost a century. Within the first period of purely academic studies of gas hydrates from 1778 to 1934, only 56 papers from 16 authors were published. There was not much interest in gas hydrates from industry prior to the 1930s.

The second period of gas hydrates study began in 1934, when Hammerschmidt published the results of the inspection of the U.S. gas pipelines. It was noted that the inspection was complicated by the formation of solid plugs in the winter time. It was assumed that they encountered ice plugs freezing from hydrotest and condensed water. Hammerschmidt, relying on his laboratory investigations, showed that the solid plugs consisted not of ice, but of hydrate of the transported gas. The urgency of gas hydrates studies grew sharply. It was necessary to investigate in detail the conditions of the formation of gas hydrates and to find an effective means of preventing solid hydrate plugs from forming in pipelines. In the mid-thirties of the last century Nikitin hypothesized that gas hydrates were clathrate compounds. A few years later Stackelberg confirmed this experimentally. There were 144 papers on gas hydrates published between 1934 and 1965.

The third period in the history of studying gas hydrates is tied to the discovery of natural gas hydrates, which will be an unconventional source of energy in the coming decades. The existence of gas hydrates in nature was proven in the 1960s. Idea about existence of natural gas-hydrates was formulate after drilling Markhinskaya well in Yakutia in 1963 and analysis of thermodynamic conditions in the reservoir. Depth of well was 1800 m, thickness of permafrost was 1200 m, temperature at 1450 m depth and the bottom of the well was 0 °C and 3.8 °C respectively.

Over 7000 papers on natural gas hydrates have been published since then. Now we know that gas hydrates exist in nature and they are present both on our planet and exist in the universe. Hydrates played an important role during the formation of planets, our atmosphere and hydrosphere.

The problem of development and production of gas from GHD is an important problem for the twenty first century. A number of countries, including the USA, Japan, India, China, Korea, Germany and others, have national programs for studying and industrial production of natural gas from hydrates. Furthermore, in many countries, including Russia, serious studies of gas hydrates are conducted in many university laboratories. However, even the basic review of publications on gas hydrates shows that most of the research projects are conducted separately, at different scientific levels, and the published results frequently are not noticed by the energy industry. The scientific community should be more focused in an effort to improve the technologies necessary to locate, to measure and to produce gas from gas hydrate deposits.

The first experience of natural gas production from hydrate deposit came from Siberia. The Markhinskaya well drilled in 1963 in the northwestern part of Yakutia to 1800 m depth, revealed a section of rock at 0°C temperature at 1450 m depth, with permafrost ending at approximately 1200 m depth. After compared the conditions of that section of rock, we recognized it matched hydrate formation conditions. This match allowed us to formulate a hypothesis of the possibility of gas-hydrate accumulations existence in cold layers. The natural hydrate hypothesis was seriously doubted by the experts. The idea needed an experimental confirmation. Hydrates of natural gas were then formed in porous medium and in real core samples at the Gubkin University laboratory in Moscow by the Author. The results have compellingly shown the possibility of formation and stable existence of naturally occurring gas-hydrates in rock layers, which was recorded as the scientific discovery of natural gas hydrates. After a comprehensive international examination, the discovery of natural hydrates was recorded in the USSR State Register of scientific discoveries as n. 75 (1969) with the following formulation: “The previously unknown property of natural gases to form deposit in the solid gas-hydrate state in the earth’s crust at specific thermodynamic conditions was experimentally established”.

Soon thereafter, a group of young geologists named Sapir, Ben’yaminovich and Beznosikov found the first gas hydrate deposit in the Messoyakha field in the Transarctic, on the eastern border of West Siberia. Comprehensive geophysical and thermodynamic studies, performed in the Messoyakha wells showed that gas is in hydrated state existed in the upper part of the deposit. The underlying part of the deposit contained gas in a free state. The Messoyakha field with original reserves of about 30 billion m^3 was dwarfed by the giant Urengoy, Yamburg and Medvezhye gas fields in Siberia. However, the Messoyakha production of gas from hydrate was a catalyst in the growth of research on natural gas hydrates in the world. The field provided gas to an important steel mill in the Transarctic, and allowed the steel mill to replace costly imported coal with the clean, cheap natural gas. The Messoyakha field was the first confirmation of the presence of gas hydrate deposits and the possibility of their commercial development. The discovery of natural gas hydrates coincided with the peak of one of the energy crises in the world. Studying gas hydrates became more important as energy prices increased in the 1970s. The basic stages of the history of the gas hydrates discovery are as follows:

1778 - Priestley obtained SO_2 hydrate in a laboratory.
1811 - Davy obtained Cl_2 hydrate in a laboratory and called it a hydrate.
1934 – Hammerschmidt studied gas hydrates in industry.
1965 – Makogon discovered natural gas hydrates as energy resource.
1970 – Start of gas production from the Messoyakha gas hydrate deposit.

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Biographical Sketch

Yuri F. Makogon had graduated with honors from the Krasnodar Technical School (1951) and the Gubkin Petroleum Institute in Moscow in 1956, starting his career that year at the Shebelinskoe Gas-condensate Field in the Ukraine. In 1963 he received M.S. degree at the Gubkin Oil and Gas Institute, followed by his D.Sc. in 1975, and professor from 1985. Dr. Makogon is a world-renowned expert on gas hydrates, with more than 45 years of experience in industry, academia and research within the oil and gas industry. He is author of scientific discovery of gas hydrates in nature; he has authored eight books and over 250 publications. He holds 27 patents. 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 in Germany. From 1974 till 1987 he served as the head of the gas-hydrate laboratory at the Central Gas Research Institute of the USSR. From 1987 to 1993, he held director’s positions at both the gas-hydrate laboratory of the Oil and Gas Research Institute Russian Academy of Science, and at the Hydrocarbon and Environment Institute of the RANSc.

Dr. Makogon co-founded the Russian Academy of Natural Science (the RANS) in 1990, serving as the first chairman of the Oil-Gas Consulate of the RANS. During 1991 to 1993, he had established and served as the first chairman of the Russian Section of the International Petroleum Engineering Society (SPE). In 2002 he was Nominated International Distinguished SPE Lecturer for 2002-2003. From 1995 he heads the gas-hydrate laboratory at the petroleum-engineering department, Texas A&M University, and serves as the Regional Secretary of the RANS, U.S. Section. His professional awards include the Gubkin State Prize (1989); the golden L. Kapitca Medal for Scientific Discovery (1997); the V. Vernadsky Medal of Honor-2000; golden A. Einstein Medal of Honor from the RANS (2002); nomination as International Man of the Year for 1992/1993 by Cambridge International Biographical Center, and the Russian Academy of Natural Sciences Honorary Merit in Science and Economics (2005). Dr. Makogon has received an honorary doctorate from the Nikolayev Institute of Inorganic Chemistry Russian Academy of Science (2005). Lifetime Achievement Award of Honor, the Sixth International Conference on Gas-Hydrates 2008 Yuri F. Makogon was born 15 May, 1930, in Ukraine. He has two children and three grand children. His hobbies include painting, traveling and photography.