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TO THE HISTORY OF GAS HYDRATES DISCOVERY

Three periods in the bicentenary history of exploration of sintezed and natural gas gydrate are described.

Keywords: *scientific achievements, clathrate, gas hydrate formation, gas hydrate fields, resources.*

Gas hydrates are clathrate compounds of water and gas molecules, stable under certain conditions of pressure and temperature. The history of gas-hydrates has three distinct periods defind by the purpose and content of the research: academic, engineering and energy.

Revealing of the truth in the history of development of any considerable scientific idea usually turns out to be very complicated. A scientist who makes a first discovery frequently would not pay proper attention to the nature of phenomenon he had revealed, especially if the discovery has no use by his contemporaries. The same phenomenon may be discovered by several scientists concurrently. Only after a long time when the new idea gets its progress strengthened by factual evidence, will the scientific society take an interest to the roots of the discovery and to the researcher himself. When the idea is considerable and important for future progress of civilization, being advanced in different parts of the world, one may be tempted to give the priority to one of national scientific schools when considering the history of discovery. But no matter what are the national interests, only one truth exists and it must reflect the real contribution of each scientific school and each individual scientist. The majority of scientific discoveries results from the outstanding work of some creative individuals searching and filling constantly the blank spaces in Science.

Gas hydrates are no exception. The boundary between 18 and 19 centuries was the time when the explosively developing industry came to acute need of science, when every new discovery had a profound impact on the pace of civilization development and the particular hopes of the society where pinned to physics and chemistry. It was then that the gas hydrates, solid molecular compounds of water with gas, were discovered.

The history of the discovery is not conventional. It is well known today there are vast hydrate accumulations on the Earth, however the first hydrates where synthesized in the laboratory. A century and a half later their technological significance was appreciated, and several decades later hydrate deposits were revealed, with their potential source of power being many times in excess of the conventional hydrocarbon resources.

Up to this point most specialists believed that gas hydrates were first obtained in 1810 in the laboratory of Sir Humphry Davy, who cooled an aqueous solution saturated with chlorine gas below 9 °C to yield some crystals of an ice like material (Davy, 1811). However a detailed analyses of the preceding work uncovered the fact that gas hydrate were known more than 30 years prior to H. Davy's work.

A report (entitled «The Discovery of Gas Hydrates» was made at the 7th International Conference on Gas hydrate by Sir John Meurig Thomas, former Director of the Royal Institution of Great Britain where Davy made his discovery). The report was disclosed to a multifaceted scientific work of Sir H. Davy, who in 1811 published his results of obtaining solid crystals formed by bubbling chlorine through the water at atmospheric pressure and temperatures slightly below 0 °C. The resulting crystals Davy called «hydrates.»

Davy did not show any interest in the results he obtained and did not return to further studies of this topic. Twelve years later Michael Faraday became interested in the crystals obtained in the laboratory where he worked as Davy assistant.

He determined the composition of chlorine hydrate (1:10, i.e. per mole of chlorine had 10 moles of water) for the first time in 1823. It was a great success taking into account the level of measuring tools of that time. Despite the fact that the name of the crystals did not reflect their content and structure the definition of «gas hydrate» is often used at present.

Past few centuries for humanity were characterized by the active development of modern civilization. Science certainly always plays a leading role in the development of mankind. A great number of substances and gases have been discovered during 17—18 centuries. The properties of gases and their possible use was actively studied in many countries around the world. One of the most talented scholars of the 18th century Joseph Priestley (1733—1804) discovered 9 gases including SO_2 (1775); N_2 (1774); NO (1772); N_2O (1774); HCl (1774); CO_2 (1774); NH_3 (1774). But in the history of science, Joseph Priestley is best known as the author of discovery of oxygen (1774).

Priestley met in London the leading men of science, including the American statesman and inventor eb://cgi-bin/g?DocF=/index/fr/ank/59.html - 4A4FJBenjamin Franklin. On the basis of his electrical experiments, Priestley in 1766 was elected to be a member of the Royal Society of London. The next year, with Franklin's encouragement and generous loan of the requisite books, he published The History and Present State of Electricity, In 1767 Priestley was appointed minister of Mill Hill Chapel, in Leeds, Yorkshire, where he had more leisure for writing and experimenting.

Concurrently with these experiments, Priestley developed rapidly as a political theorist. Throughout his life Priestley was an ardent believer in human progress and perfectibility.

In 1767, Priestley settled down in Leeds, where he began his experiments with gases. So many gases were already discovered by that time. J. Priestley paid a lot of attention to the discovery by him of sulphur dioxide in 1775.

Studying in particular the solubility of SO_2 in water at atmospheric pressure and temperatures around 0 °C, in 1778. That was a solid, non transparent crystals and he determined their density (the crystals were drowned in the water), revealed the influence of water on the conditions of formation and decomposition of the crystals in a solution of SO_2, i.e. first paid attention to the possibility of inhibition processes, but did not name the resulting crystals consisting of molecules of gas and water «hydrates».

Priestley had an opportunity to realize, in the frosty winter of 1778, in London, that «...water impregnated with vitriolic acid air (i.e. SO_2 — auth. remark) may be converted into ice...». «I exposed in an open vial a quantity of water fully impregnated with vitriolic acid air, when the thermometer was at 17 degrees (i.e. – 8.3 °C — auth. remark), and observed that it was recently frozen quite through, the smell of it continuing to be very pungent. As it melted, the ice sunk to the bottom of the liquor, and when it was quite dissolved, the water appeared to be still very strongly impregnated. Ice was not at all dissolved in vitriolic acid air. Letting it remain in this situation all night, the next morning I found all the air absorbed; but it appeared, by the form of the ice, that it had been melted, and frozen again; for it exactly fitted the glass vessel in which it was confined» (Priestley, 1790).

J. Priestley also found the «ice» to decompose when put in an atmosphere of HCl, NH_3 and HF under the atmospheric pressure and low temperatures, and to remain stable under the same conditions in the air. Thus the effect of hydrate inhibition was properly recognized.

Joseph Priestley was a highly curious and effective investigator. Nine new gases were discovered by him, with oxygen, hydrogen, carbon and sulphur dioxides among them. SO_2 is well known to date to form hydrate easily under atmospheric pressure and temperature of +6 °C. It is these conditions that allowed Priestley to obtain the SO_2 hydrate. However no serious importance was attached by him to the discovery because there was no theoretical or practical value he could derive from it.

There is some evidence that the SO_2 — hydrate had been obtained by at least three researchers following Priestley and prior to Davy: T. Bergman (1783), A.F.de Fourcroy and L.N. Vauquelin (1796, 1798), A.F.de Fourcroy (1801) (Gmelins Handbuch, 1960).

It should be noted that the repeated discovery of gas hydrates by Humphrey Davy during his experiments on the chlorine and its aqueous solutions also caused no enthusiasm both among scientists and industrialists. H. Davy, never returned to the studies on hydrates. However, his disciple, later the great physicist, Michael Faraday in 1823 made a replica of his patron's experiment to obtain a composition formula of the chlorine hydrate: $Cl_2 \cdot 10H20$. Several years later the SO_2 hydrate composition of $SO_2 \cdot 7H_20$ was gained by de la Rive (1829). It should be mentioned that the SO_2 hydrate primary obtained by Priestley had attracted the attention of scientists in the 19 th century. It was the SO_2 hydrate on which the quadruple points of the equilibrium curve were first obtained by Roozeboom (1884, 1885) . The measurement techniques of that time did not allow precise results to be obtained. Thus J. Pierre in 1848 showed the hydrate composition as $SO_2 \cdot 11H_20$ (Pierre, 1848) whereas Schoenfeld reported it in 1855 to be $SO_2 \cdot 14H_20$ (Schoenfeld, 1855). Only in 1927 the correct formula was given by W. Schroeder, who obtained the complete SO_2 hydrate phase diagram: $SO_2 \cdot 6H_2O$ (Schroeder, 1927).

Hydrate SO_2 and Cl_2 can be formed at atmospheric pressure for t >0 °C. The heat of hydrate formation data at t ~ 0 °C are 69.3 and 66,9 kJ/mole, and density of the hydrate 1.17 and 1.197 g/cm^3 respectively, (Hagan, 1962).

In 1780 Priestley moved to Birmingham taking the lab of Watt. He had a solid independent nature. He supported the French Revolution and he was critical of the Church

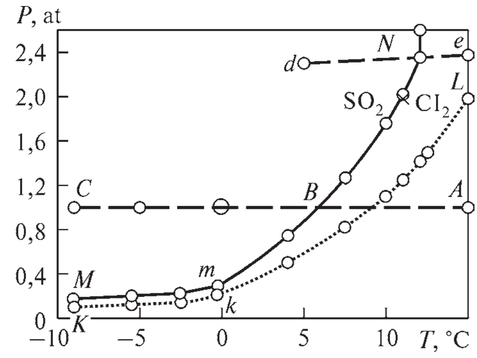

Fig.1. SO_2 and Cl_2 water hydrate P-T equilibrium

of England. He received French citizenship, and at the same he got a great opposition from his colleagues. Their relationship became worse and worse. In 1791, on 14 July (anniversary of the storming of the Bastille), his house was set on fire. In 1794 he migrated to the United States, where he died 10 years later.

Gas hydrate was first obtained by J. Priestley (1778) while bubbling SO_2 through water at a temperature close to 0 °C and atmospheric pressure. However Priestley did not call them «hydrates» describing obtained crystals. Only 33 years after Davy obtained a chlorine hydrate in a similar way and called it «hydrate». It should be emphasized: the moral beliefs of researchers and political arguments can not affect the interpretation of the history of scientific discoveries.

Academic studies of hydrates of different gases continued from 1778 to 1934. During this period 44 works by 17 authors have been published. The results have not found wide commercial use. People have not found any application for them and their research have evolved spontaneously. However, the results of academic studies were important for initiation of engineering studies of gas hydrates.

20 th century is characterized by intensive development of industry with high energy consumption of mineral sources: coal, oil and natural gas. Oil and gas reservoirs are usually located at large distances from the consumers. So they have to be transported by pipeline under pressure. Solid plug can be formed dramatically complicating the transport of gas in winter and spring periods. It was believed that was the ice that formed plugs in gas pipelines from condensate water. Industry did not know gas hydrates at that time. Important work were published in the US in 1934 on the basis of experimental studies (Hammerschmidt, 1934), which showed solids that being formed in pipelines were hydrates. This work gave impetus to studies of gas hydrates in the industry in order to prevent hydrate formation and elimination of the clusters in the pipeline and use the properties of hydrates in various technologies. During the period 1934—1965 there were published 143 works.

The third period in the history of exploration of gas hydrates is associated with the discovery of the existence of natural gas hydrates, which played a leading role in the formation of planets, the atmosphere and hydrosphere of the Earth, but were not known.. Natural gas hydrates is are source of mineral energy. The first assumption of the existence of gas hydrate deposits in permafrost regions of Canada in 1943 was made by Donald Katz, professor of the University of Michigan, but attempt to prove by well drilling was not successful (Katz, 1982). Again in 1946, a similar assumption was made by Strizhov, prof. of Russian Gubkin of Oil Institute, but he did not have any evidence. Moreover, he expressed pessimism about the feasibility of their development.

Author PhD thesis (1962) was the first PhD one in the history in the gas hydrate field. The present author's visit to the Markha well (1963, depth 1800 m, Yakutiya), revealed that the rocks were at temperature of 0 °C at the depth of 1450 m, This author suggested that hydrates may exist in a cold layers (Makogon, 1965). The hypothesis needed to be verified experimentally. For this purpose a series of direct experiments on hydrate formation and dissociation in natural and artificial core samples was set up by Makogon at Gubkin Russian State University of Oil and Gas. The main results of these experiments and first theoretical summaries were published in 1965—1966. Results of experimental studies of hydrate formation and decomposition of real cores were presented at a scientific conference of young professionals in Moscow in April 1965 and awarded the first prize.

After a comprehensive international assessment and a close scientific examination those results and summaries of the Presidium of the Academy of Sciences, 24th December 1969 were registered in the USSR State Register as scientific discovery No. 75, which proclaimed: «Experimentally proved earlier unknown property of natural gases a form solid hydrate deposits in the Earth's crust under certain thermodynamic conditions»

At the same time, December, 1969 in the Arctic region in Siberia, the first gas hydrate field Messoyakha was put into production.

The author's report about laboratory and industrial results on gas hydrate research, was presented on the 11 International Gas Congress and 8-th World Oil Congress, Moscow 1970; 1971, attracted great international attention. Soon, several countries have established national program of research and development of hydrate deposits. As a result of intensive investigations over several years methods of survey and prospecting of both on — and offshore hydrate deposits were devised, as well as method of estimation of hydrate gas resources.

The energy component of natural gas hydrates prompted the start of active research development of gas hydrate formation conditions research in porous media and their properties. Research laboratories have been established in short time in the USSR, USA, UK, Canada, Japan, India, Norway, Germany, China, South Korea and others, which have deployed specialized studies of natural gas hydrates. As a result, an effective means of prospecting, exploration and development of hydrates has been created: promising areas for prospecting have been identified, methods to identify the intervals of occurrence of hydrate reservoirs offshore and onshore, methods for the determination of gas reserves in hydrate state have been proposed, potential resources and recoverable reserves of gas hydrate have been calculated. The number of publications on gas hydrates has increased dramatically and exceeded 12 000 for the period 1965—2012.

Today we have over 250 gas hydrate fields in the world. Potential resource of gas in hydrate state $1{,}5 \cdot 10^{16}$ m^3. About 97% of gas hydrate deposits in offshore, and 3 % in onshore. In one m^3 of hydrate contents 164 m^3 of methane, and 0.8 m^3 of water.

We have good experience of commercial development of gas hydrate deposits. Same time we have many serious scientific and industrial problems, that should be solved.

Conclusion

It is known that history is made by one people, the others write about it, and the third people study and interpret, depending on the political situation. In this paper, the author attempt to find out the real history of the initial period of gas hydrate research.

I thank Sir John Meurig Thomas for useful suggestions and comments. I also thank Roman Y. Omelchenko for his assistance in preparing the initial manuscript.

REFERENCES

1. *Priestley, J.,* 1778—1780. Versuche und Beobachtungen Uber Verrshiedene Gattun-gen der Luft, Th. 1—3, 3:359—362. Wien-Leipzig.
2. *Priestley, J.* 1790. Experiments and observations on different kinds of air, and other branches of natural philosophy, connected with the subject. Birminham, Thomas Pearson. 2:359—362.
3. *Davy H.* 1811 Phil. Trans. Roy. Soc. London. 101/ — p.1357.
4. *Hagan S.* Martinette, 1962 London, Clathrate Inclusion Compounds
5. *T. Bergman* (1783), A.F.de Fourcroy and L.N.Vauquelin (1796, 1798), A.F.de Fourcroy (1801) (Gmelins Handbuch, 1960)
6. *Faraday M., Phil.* Trans. Roy. Soc. London, 113/ — 160 (1823)
7. *Gregory, J.* Craven, The scientific achievements of sir H. Davy, Oxford univ. press; London, Milford, 1930.
8. *Roozeboom, H.W.B.*1884. Rec. Trav.Chem. Pays-Bas.3:26.
9. *Roozeboom*, *H.W.B.*1885. Rec. Trav.Chem. Pays-Bas.4:65.
10. *Pierre J.* 1848. Ann.Chem. Phys. Ser. 3 23:416.
11. *Schoenfeld*, *F.A.* Ch. 1855. Neue Reihe. 19:19.
12. *Schroeder, W.* 1927. DieGeschichte der Gas Hydrate. Chem. V.29/ — p. 98.
13. *Hammerschmidt, E.G.* 1934. Formation of gas hydrates in natural gas transmission lines. Ind. Eng. Chem. 26:851—855
14. *Katz D.* 1988, Private communication (see letter, attach file)
15. *Strizhov I.N., and Khodanovich I.* 1946, Gas Production, GTTI, Moscow, p. 376
16. *Makogon Y.F.*, 1965. A gas hydrate formation in the gas saturated layers under low temperature., Gazovaya Promyshlennost (Gas Industry), No.5. p. 14—15.
17. *Makogon Y.F.*, 1966. Characteristics of Gas Field Development in Permafrost, TsNTI MinGazProm, Moscow, Russia, 20 pp.
18. *Makogon Y.F.* 1974; Hydrates of Natural Gases, NEDRA, Moscow; 1981, PennWell, Tulsa, pp. 237
19. *Makogon Y.F.*, 1997. Hydrates of Hydrocarbons, PennWell, Tulsa. pp. 482.

Статья поступила 27.01.2014

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К ИСТОРИИ ОТКРЫТИЯ ГАЗОГИДРАТОВ

Описаны три периода в 200-летней истории изучения синтезированных и природных газогидратов.

Ключевые слова: *научные исследования, клатраты, гидратообразование, газогидратные залежи, ресурсы.*

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ЩОДО ІСТОРІЇ ВІДКРИТТЯ ГАЗОГІДРАТІВ

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