AGH DRILLING, OIL, GAS • Vol. 33 • No. 4 • 2016

http://dx.doi.org/10.7494/drill.2016.33.4.811

Hennadiy V. Zhuk*, Oleksandr I. Pyatnichko*, Viktor T. Krushnevich*, Denys S. Fedorenko*, Vasyl V. Klymenko**

METHANE HYDRATE TECHNOLOGIES IN UKRAINE: RESEARCH AND PROSPECTS***

1. INTRODUCTION

The problem of natural gas hydrates in the world has been studied relatively recently-for about twenty years. The USA intensified investigations in this field. In 2001 "Act concerning hydrates study" was adopted. The USA government gave 50 million dollars for research. Japan, Canada, Korea, India also took part in this study.

According to the studies performed by the Institute of Geological Science of the National Academy of Science of Ukraine in 1990s in terms of Order of the Cabinet of Ministers of Ukraine No. 938 (22.11.1993) "On gas hydrates raw material exploration in the Black Sea and creating effective technologies of its production and processing", three zones of hydrate formation with estimated reserves of 50–60 trillion cubic meters of methane were found out in the Black Sea. According to their estimation, one of the multilayered structures only from one horizon can produce 40–60 billion cubic meters of gas if production ratio is 10% [1].

Gas hydrate technologies compared with existing ones, gives the possibility to transport gas, divide gas and liquid mixtures, compress gas up to great pressure, concentrate water solutions, produce and accumulate cold, utilize and store CO_2 etc. with greater efficiency. Their study is also very important to solve the problem of developing methane gas hydrate deposits, particularly, within Black Sea aquatorium [2].

However, methane production technologies have not developed industrially and their study was performed with the help of experimental units and in separate gas hydrates deposits in the mode of tests and elaborations [3–6].

* Gas Institute of National Academy of Science of Ukraine, Kyiv, Ukraine
** Kirovohrad National Technical University, Kirovohrad, Ukraine
*** Paper prepared within of the report on the First Ukrainian Scientific and Technical Conference "Gas Hydrate Technologies in Mining, Oil and Gas Industry, Geotechnics and Energetics" (Poltava, 2014, Ukraine)

Test results concerning the technology of producing hydrate/ice-gas hydrate granules and natural gas transportation in the form of hydrates are known only on the basis of studies performed with the help of experimental and breadboard installations [7–9]. Japanese companies have developed the technology of hydrate granules production, generated and successfully tested the chain: granules production – delivery with the help of automobile transport – gas usage to produce electric power (heating) [9]. Natural gas overseas transportation in the form of hydrates from the deposit to the consumer was substantiated [10, 11].

Carbon dioxide disposal having a greenhouse effect in the form of hydrates is prospective. It has been already mentioned by the authors in previous papers [12, 13]. It is necessary to note that the government of Australia, Canada, Japan, Norway, Korea, Great Britain and the USA as well as European Commission financed and actively promoted large projects to demonstrate the technologies of carbon dioxide capture and storage (Carbon Capture and Storage – CCS). By April, 2010 state investment of capital was in the range of 26.6–36.1 billion US dollars. Moreover, the government promised to launch from 19 to 43 large-scale projects of carbon dioxide deponation up to 2020.

At present, the Ukraine is very interested in developing gas hydrate technologies for the fields of study mentioned above. Methane production from natural gas hydrates will enable the reduction of a great part of natural gas import deliveries and to give up them completely in the future. Natural gas transportation in the form of hydrates is also urgent as a competitive alternative to its transportation in a liquid state.

To analyze the present state of studies in the field of methane hydrate technologies and determine prospects for their usage in the Ukraine, to estimate experimentally possibilities methane replacement technology in hydrates by carbon dioxide.

2. BASIC RESEARCH PRESENTATION

Methane production from natural hydrates

Predictable technologies of methane production from its hydrates is based on thermodynamic balance disturbance within the system methane-water-methane hydrate with the help of the local temperature increase, pressure decrease, addition of the third active element (liquid or gas). The first two ways are rather expensive due to the absence of confined (localized) space: temperature and pressure differences as for the environment should be constantly maintained. Moreover, maintenance cost probably will exceed power profitability in terms of methane production. The methanol supply to the well was experimentally tested in the Messoyahsk deposit in order to increase gas production thanks to hydrate decomposition [3]. Well yield was increased, but technological expenses have exceeded the economic effect of methane production.

A great number of scientists believe that the most promising method of developing gas hydrate deposits is methane replacement within hydrates by carbon dioxide [14].

There are all conditions (thermodynamic, power, structural) to replace methane molecules in hydrate composition by carbon dioxide molecules. Carbon dioxide hydrates are formed at a lower pressure than methane hydrates if sea water temperature is from 0 to 8°C [12]. Dissociation heat of methane hydrates is approximately equal to the carbon dioxide hydrates formation/dissociation (numerical values are various in some extent in different papers – Tab. 1), that is, replacement process does not demand additional heat supply.

Natural gas transportation in hydrate state

Technology of gas transformation into hydrate state is paid not less attention to than methane production from natural hydrates.

Table 1

Hydrate dissociation heat CO_2 and CH_4 [kJ/mol]

Data source	CO_2	CH_4
[15]	–	54.2
[16]	59.9	60.67
[17]	68.9	–
[18]	–	64.5

Pilot testing of hydrate technology of capsules (pellets) production composed of methane and water hydrates was successfully performed. Production of hydrate capsules with productivity of 0.7 ton per day was started [9]. The cost estimation of hydrate method of natural gas transportation was determined [11].

According to this technology [9], gas is converted into gas hydrates one ton of which contains about 160 standard cubic meters of methane. Natural gas is purified against CO_2 and H_2S and when it contacts with water, hydrates in the form of granule are produced. Granules are stored within the tank and delivered by the sea in containers at – 20°C temperature. In the port of destination they are discharged into the tank and when it is required they are reloaded into cisterns of high pressure. Then they are delivered to the entrance of the gas main pipeline. Hydrate regasification by means of dissociation (decomposition) under the action of external heating is performed before injection into the main pipeline.

Hydrate capsules (Fig. 1) or blocks are transported by the sea if pressure is up to 0.5MPa and the temperature is 253 K [9]. It corresponds to the temperature of the maximal methane hydrate stability. At a temperature below water freezing natural gas hydrates can be stored if the pressure is close to the air one, that is, it is much less than balance pressure (so called hydrates "selfconservation" [19]). Ice-gas hydrate capsules can be stored and transported if air pressure and temperatures are 263–258 K [2].

Fig. 1. The form of hydrate capsules within the container

Mitsui, a Japanese company has implemented a pilot project of gas supply (1,000 standard cubic meters per day) of the small gas-turbine power station with 280 kW capacities.

Experimental estimation of methane gas hydrates replacement by carbon dioxide with the help of the express method

In Ukraine the beginninsg of a gas hydrate study (crystalline hydrates) and their technological application were highlighted in the papers of L.F. Smirnov [20, 21], A.S. Cheptsov [22], V.V. Klymenko [24]. Experimental studies of hydrates were performed in the Odessa Institute of Low-Temperature Technique and Power Engineering (freon hydrates R-12 and R-22) [23, 25], Institute of Colloid Chemistry and Water Chemistry of the National Academy of Science of the Ukraine (freon hydrates R-12) [22], Kirovograd National Technical University (carbon dioxide hydrates and ice-gas hydrate capsules) [26, 27]. Since 2009 methane hydrates of natural gas have started to be studied with the help of special equipment at the National Mining University [28].

In order to study the formation and dissociation hydrates of carbon dioxide compounds which are the part of natural gas, the Institute of Gas has made hydrate stand SG-16:100 [12]. The express method of determining thermodynamic and kinetic parameters of hydrate transformation was tested with the help of hygrometer TOROS-3-2 VIZ of in-house design (Fig. 2).

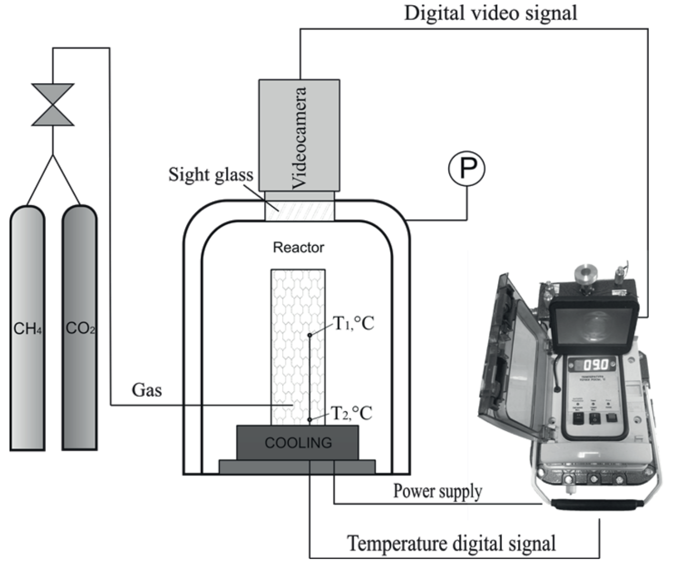

Fig. 2. Equipment for the hydrate study with the help of the express method

The main hydrometer function is to measure the water dew-point within natural gas if the operating pressure is up to 25.0 MPa within various gases (natural gas, hydrogen, air, nitrogen, carbon oxide, helium etc.) if dew-point temperature is from minus 65 to 20°C with ± 0,5°C basic absolute accuracy. Applying the lithium-phosphate accumulator of the new generation was able to reduce hydrometer weight and provide the performance up to 800 measurements in autonomous mode.

To accelerate the process of hydrates formation hydrometer operating chamber was equipped with bubbler.

The express method is the following. Water temperature within the bubbler is predominantly higher than the balance one. Then the temperature is gradually reduced at the same gas bubbling. Gas is delivered from the cylinder under 15–18 MPa pressure. The required pressure is maintained in terms of operating volume with the help of a pressure reduction valve. Gas is additionally cooled within intermediate chamber–thermostat up to the necessary temperature. In terms of constant bubbling water temperature is reduced till hydrates production (Fig. 3).

a) b) c)

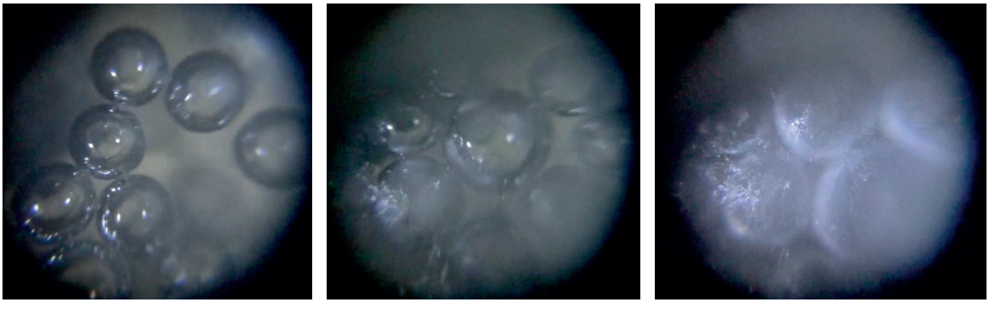

Fig. 3. Methane hydrates formation within the bubbler:
a) state before hydrates formation; b) formation start; c) transition into hydrate state

By means of averaging water and gas temperature in terms of pressure setting within bubble chamber thermodynamic conditions of hydrates formation for a given technologic scheme were determined. The presence of hydrate components of natural gas within the bubble is confirmed by atmosphere burning in the open air above the solid phase (Fig. 4).

a) b)

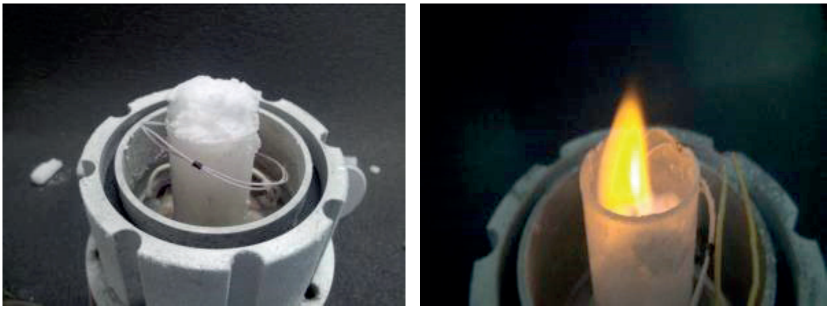

Fig. 4. Hydrates in the working chamber:
a) fixation at a −40°C temperature; b) gas burning from dissociation hydrate

Natural gas hydrates as well as carbon dioxide hydrates were produced with the help of the express method. Natural gas hydrates were produced within the reactor by pressure increase till balance one. To fix the hydrate state (solid phase) a reactor was first cooled outside with the help of solid carbon dioxide up to –40°C. Then the pressure within the reactor was reduced till air one bleeding excess natural gas.

After that the working volume of the reactor was heated again up to complete gas dissociation. While performing experiments it was determined that the composition of original natural gas and gas liberated in terms of hydrate decomposition is of great difference (Fig. 5). This fact is explained by the difference of the balance conditions of hydrates formation for natural gas components. While cooling and in terms of pressure increase hydrate formation of heavier hydrocarbons takes place earlier [16].

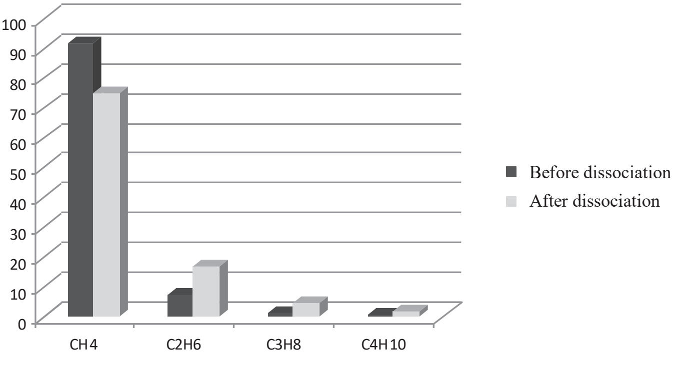

Fig. 5. Natural gas composition before hydrates formation and after their dissociation

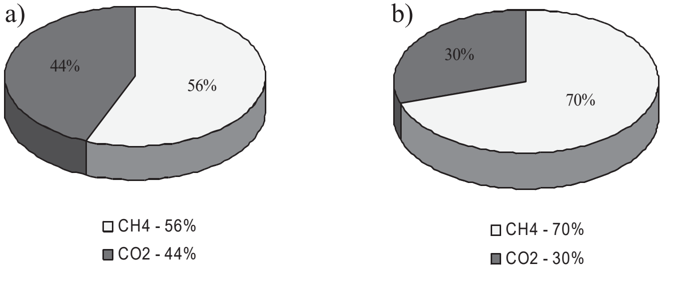

Fig. 6. Composition of gaseous phase above hydrate:
a) immediately after blowing with the help of carbon dioxide gas; b) after two hours

Thus, “selective” hydrates formation of natural gas formation is performed.

A set of experiments was also performed to study the process of methane replacement with the help of carbon dioxide. It was showed that after natural gas hydrates production, as it was described above, its inflow was stopped and the bulb with carbon dioxide was connected to the reactor. Carbon dioxide (up to five volumes of reactor) was blown-down above the surface of the hydrate mass. Then all the valves were shut and air sample was taken to test. Furthermore, the reactor was held at a constant temperature and pressure for two hours and an additional sample was taken.

According to the gaseous phase analysis, 14% increase of methane content was fixed. This fact proves its replacement in hydrates with the help of carbon dioxide.

3. CONCLUSIONS

This analysis confirms work prospectivity in the field of hydrates technologies in Ukraine. The study of hydrate sea deposits and the developing technology of methane production can be performed by joint efforts of universities and research institutions in Ukraine with the attraction of gas production enterprises and foreign organizations. The possibility of using such technology to develop gas hydrates deposits in the Black Sea was confirmed by the positive results of experimental study performed with the help of the express method of methane replacement by carbon dioxide in gas hydrates. Within the next few years it is possible to develop innovative experimental-industrial equipment to transform natural gas into hydrate state, its transportation and regasification.

REFERENCES

[1] Sokur O.M.: *Hidratoutvorennya v Chornomu mori*. Zbirnyk naukovykh prats' instytutu heolohichnykh nauk NAN Ukrayiny, 2009, 2, pp. 141–146.

[2] Klymenko V.V.: *Naukovo-tekhnichni osnovyhazohidratnoyi tekhnolohiyi (termodynamika ta kinetyka protsesiv, skhemni rishennya*. Thesis abstract of the doctor of technical science, 05.14.06, Kyiv 2012.

[3] Makogon Yu.F.: *Prirodnyye gazovyye gidraty: rasprostraneniye, modeli obrazovaniya, resursy.* Rossiyskiy Khimicheskiy Zhurnal, no. 3, 2003, pp. 70–79.

[4] Borodin K.: *V Yaponii nachat pervyy v mire eksperimentpo dobyche metanogidratov.* http://energo-news.ru/archives/90046/16.02.2012.

[5] Borodin K.: *SSHA i Yaponiya proveli testovoye izvlecheniye prirodnogo gaza iz metanogidratov v Arktike.* http://energo-news.ru/archives/108879.

[6] *Yaponiya zabezpechyt' sebe palyvom z hazohidrativ.* http://ua.euronews.com/2013/03/12/ japan-joins-the-dash-for-gas-but-at-what-price-for-the-atmosphere/.

[7] Skripnik A.V., Klimenko V.V.: *Eksperimentalnaya otsenka protsessov zamorazhivaniya smesi „N2O H_2O + gazovyye gazovyye gidraty CO_2".* Kholodylna tekhnika i tekhnolohiya, no. 1(105), 2007, pp. 87–89.

[8] Biletskyy V.S., Pedchenko L.O., Pedchenko M.M.: *Tekhnolohiya formuvannya hazohidratnykh blokiv z metoyu transportuvannya ta zberihannya vuhlevodnevykh haziv*. Visti Donetskoho Natsionalnoho universytetu, no. 1(30) 2(31), 2012, pp. 363–372.

[9] Shigeru Watanabe, Shinji Takahashi, Hiroshi Mizubayashi: *Demonstration Project of Ngh Land Transportation System.* Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008). http://www.nghjapan.mes.co.jp/topics/pdf.

[10] Gudmundsson J.S., Hveding F., Borrehaug A.: *Transport of Natural Gas as Frozen Hydrate.* Proceedings 5th International Offshore and Polar Engineering Conference, The Hague, June 11–16, 1995, vol. 1, pp. 282–288.

[11] Kanda H.: *Economic Study on Natural Gas Transportation with Natural Gas Hydrate (Ngh) Pellets.* 23rd World Gas Conference, Amsterdam 2006, http://igu.dgc.dk/html/wgc2006/pdf/paper/add10399.pdf.

[12] Bondarenko B.Y., Pyatnychko A.Y., Zhuk H.V.: *Hydratnoek hranenye uhlekysloho haza*. Energotekhnologii i resursosberezheniye, no. 3, 2011, pp. 52–54.

[13] P’yatnychko O.I., Zhuk H.V., Kovalchuk V.H., Klymenko V.V.: *Zamishchennya metanu dyoksydom vuhletsyu v pryrodnykh hidratakh Chornoho morya*. Zbirnyk naukovykh prats’ za materialamy IU Vseukrayins’koyi naukovo-praktychnoyi konferentsiyi „Problemy y perspektyvy rozvytku akademichnoyi ta universytets’koyi nauky”, 8–9.12.2011, Poltava: PoltNTU, pp. 61–63.

[14] Nago A., Nieto A.: *Natural Gas Production from Methane Hydrate Deposits Using CO_2 Clathrate Sequestration: state-of-the-art review and new technical approache.* Hindawi Publishing Corporation: Journal of Geological Research, vol. 2011, Article ID 239397, p. 6.

[15] Istomin V.A., Yakushev V.S.: *Gazovyye gidraty v prirodnykh usloviyakh*. Nedra, Moskva 1992.

[16] Byk S.Sh., Makogon Yu.F., Fomina V.I.: *Gazovyye gidraty*. Khimiya, Moskva 1980.

[17] Groysman A.G.: *Teplofizicheskiye svoystva gazovykh gidratov*. Nauka, Novosibirsk 1985.

[18] Makogon Yu.F.: *Gidraty prirodnykh gazov*. Nedra, Moskva 1974.

[19] Melnikov V.P., Nesterov A.N., Podenko L.S., Reshetnikov A.M., Shalamov V.V.: *Metastabilnyye sostoyaniya gazovykh gidratov pri davleniyakh nizhe davleniya ravnovesiya led–gidrat–gaz*. Kriosfera Zemli, vol. 15, no. 4, 2011, pp. 80–83.

[20] Martynovsky V.S., Smirnov L.F.: *Conversion of saline sea water to fresh by the hydrate method*, 12th International Congress of the Refrigeration, Comissien 6 B, Madrid, 1967. Bulletin of International Institute of Refrigeration, 1967, pp. 1–7.

[21] Smirnov L.F.: *O novykh tekhnologiyakh, ispolzuyushchikh gazogidraty*. Teoreticheskiye osnovy khim. tekhnoogii, no. 6, 1989, pp. 806–822.

[22] Cheptsov A.S.: *Issledovaniye protsessa opresneniya shakhtnykh vod gazogidratnym metodom.* Disstertation abstract. Candidate of technical science. ICCCW, Kyiv 1971.

[23] Klimenko V.V.: *Issledovaniye teploispolzuyushchi khkristallogidratnykh opresnitelno-kholodilnykh ustanovok*. Dissertation Candidate of technical science. Odessa Technology Institute of Refrigeration Industry, Odessa 1977.

[24] Klimenko A.P.: *Klatraty(gidraty gazov)*. Naukova dumka, Kyiv 1989.

[25] Smirnov L.F.: *Eksperimentalnoye issledovaniye protsessov obrazovaniya gidratov freona-12*. Kholodilnaya tekhnika, no. 2, 1973, pp. 28–34.

[26] Skrypnik A.V., Klimenko V.V.: *Eksperimentalnaya otsenka kinetiki obrazovaniya gidratov dioksida ugleroda v sisteme $H_2O + CO_2$*. Kholodilnaya tekhnika i tekhnologiya, no. 4 (102), 2006, pp. 50–54.

[27] Klimenko V.V., Skripnik A.V.: *Eksperimentalnoye issledovaniye plavleniya ldogazgidratnykh kapsul*. Kholodilnaya tekhnika i tekhnologiya, no. 5, 2010, pp. 54–57.

[28] Bondarenko V.I., Ganushevich K.A., Say Ye.S.: *K voprosu skvazhinnoy podzemnoy razrabotki gazovykh gidratov*. Naukoviy visnik NGU, no. 1, 2011, pp. 60–66.