Structural Features and Composition of Hydrates of Natural Gases of Certain Fields in Yakutia

L. P. KALACHEVA, E. YU. SHITS, A. F. FEDOROVA and A. M. PROTOPOPOVA

Institute for Petroleum and Gas Problems, Siberian Branch of the Russian Academy of Sciences, Ul. Oktyabrskaya 1, Yakutsk 677891 (Russia)

E-mail: lpko@mail.ru

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Abstract

Based on data for component composition of the source natural gas, external pressure, and temperature, the structure of hydrates of natural gas has been found for the main gas and oil fields of Yakutia. It has been determined that the total amount of gas in 1 L of gas hydrate ranges from 160 to 250 L.

INTRODUCTION

Two centuries have already passed from the moment of publication of the first message about obtaining a solid crystalline hydrate of chlorine; however, the problem of gas hydrates still remains urgent today. This is related to the fact that natural gas hydrates are considered as alternative sources of hydrocarbon raw owing to the high specific concentration of gas in natural hydrates (up to 160 m^3/m^3) and to a shallow occurrence of such accumulations. In addition, natural gas hydrates keep their stability both at low temperatures under conditions of permafrost on the land and under low temperature and high-pressure regime that is typical for the near-bottom part of sedimentary stratum of deep-water areas of the World Ocean. According to available calculated data, there are huge reserves of natural gas that is accumulated in the gas hydrate phase. For comparison, the reserves of natural gas in the world constitute $1.2 \cdot 10^{14}$ m^3, whereas the content of gas in gas hydrates is valued within the limits of $2 \cdot 10^{14}$–$7.6 \cdot 10^{18}$ m^3 [1].

The purpose of this work is the determination of the structure and composition of gas hydrates as well as an estimate of a free volume of gas in the hydrates that are formed by natural gas in certain gas and oil fields (GOF) of Yakutia.

EXPERIMENTAL

Gas hydrates were synthesized from distilled water and natural gas of various Yakutia GOF in a high pressure chamber at the pressure of 1.2 MPa and the temperature of 268 K during 20 days. The chamber consists in a thick-walled cylinder from plexiglas (the inner diameter of 55 mm, the external diameter of 75 mm, the height of 150 mm). The cylinder is clamped from its butts by steel flanges. Fastened separately in the flanges of the barrel is an exemplary manometer of the MO-160 type (the accuracy class of 0.4) and a gate for gas injection.

Component composition of natural gas has been studied by a gas solid chromatography method on a Crystal 2000M chromatograph. The analysis of gas for its content of methane, ethane, propane, butanes, pentanes, carbon dioxide, and nitrogen was conducted with the use of columns from stainless steel (the length of 2 m, the inner diameter of 2 mm, fillers: HayeSepN (80/100 mm) and zeolite CaA (0.25–0.315 mm)). Gas carrier was helium; the flow of gas carrier was 15 mL/min. The quantity of hydrogen and helium was determined in a column from a stainless steel (the length of 3 m, the inner diameter of 3 mm, the filler – zeolite CaA (0.25–0.315 mm)), gas carrier – argon, and the flow of gas carrier – 30 mL/min.

TABLE 1

Component composition of natural gas of certain fields in Yakutia

Fields	Composition, mol. %												
	CH_4	C_2H_6	C_3H_8	i-C_4H_{10}	n-C_4H_{10}	i-C_5H_{12}	n-C_5H_{12}	C_6H_{14}	C_{5+}	CO_2	N_2	H_2	He
Srednebotuobinskoye	85.9	7.32	2.24	0.26	0.68	0.17	0.24	0.08	0.49	0.05	2.64	0.14	0.28
Taas-Yuryakhskoye	86.1	4.7	1.52	0.18	0.44	0.13	0.25	–	0.38	0.08	6.13	0.04	0.43
Botuobinskoye	79.68	5.28	1.84	0.27	0.46	–	–	–	0.29	–	11.7	0.08	0.38
Machchobinskoye	84.65	3.36	1.26	0.17	0.32	0.09	0.09	0.06	0.24	–	9.10	0.11	0.79
Nelbinskoye	85.79	4.16	1.52	0.16	–	–	–	–	0.42	–	7.16	–	0.33
Verkhnevilyuchanskoye	90.35	2.84	0.89	0.08	0.15	0.02	0.03	0.04	0.09	0.02	5.39	0.09	0.10
Irelyakhskoye	88.86	2.25	0.97	0.12	0.22	–	–	–	0.04	0.04	7.14	–	0.36

Note. The blank implies that the given component is absent from natural gas.

TABLE 2

Molar mass of hydrate-forming gases and their hydrates

Parameters	Srednebotuobinskoye	Taas-Yuryakhskoye	Botuobinskoye	Machchobinskoye	Nelbinskoye	Verkhnevilyuchanskoye	Irelyakhskoye
M	18.61	17.71	18.86	18.15	18.02	15.92	17.55
M_{hydr}	126.61	125.71	126.86	126.15	126.02	123.92	125.55

Quantitative analysis of gases was conducted by an absolute graduation method.

RESULTS AND DISCUSSION

The total amount of gas V_g (in m^3) in a hydrated state is expressed by the equation [2]

$$V_g = 22.4 \cdot 10^{-3} V_h \rho_h / M_h \quad (1)$$

where V_h is the hydrate volume, mL; ρ_h is the hydrate density, g/mL; M_h is the molar mass of hydrate, g/mol.

The density of gas hydrates ρ can be evaluated from the sizes of the unit cell from the following empirical formulae [3]:

for the structure I:

$$\rho_I = (46M_{H_2O} + 2M\theta_{is/b} + 8M\theta_{il/b})/(a_I^3 N_A) \quad (2)$$

for the structure II:

$$\rho_{II} = (136M_{H_2O} + 16M\theta_{is/b} + 8M\theta_{il/b})/(a_{II}^3 N_A) \quad (3)$$

where M_{H_2O} is the molar mass of water, g/mol; M is the molar mass of hydrate-forming gas, g/mol; $\theta_{is/b}$, $\theta_{il/b}$ are the packing degrees for small and large bags; a_I, a_{II} are the parameters of the cubic crystal lattice of the hydrate of the respective structures I and II, nm; N_A is Avogadro's number.

The molar mass of hydrate-forming gas and its hydrate as well as the bag packing degree for the gas hydrate can be calculated based on

TABLE 3

Bag packing degree in hydrates

Fields	Structure I		Structure II	
	$\theta_{is/b}$	$\theta_{il/b}$	$\theta_{is/b}$	$\theta_{il/b}$
Srednebotuobinskoye	0.9572	0.9947	0.9445	0.9995
Taas-Yuryakhskoye	0.9540	0.9943	0.9403	0.9946
Botuobinskoye	0.9570	0.9960	0.9444	0.9986
Machchobinskoye	0.9612	0.9947	0.9492	0.9978
Nelbinskoye	0.9595	0.9944	0.9470	0.9979
Verkhnevilyuchanskoye	0.9725	0.9891	0.9639	0.9987
Irelyakhskoye	0.9642	0.9951	0.9521	0.9990

TABLE 4

Density of the synthesized gas hydrates, g/mL

Fields	Structure I	Structure II
Srednebotuobinskoye	1.400	0.899
Taas-Yuryakhskoye	1.388	0.892
Botuobinskoye	1.404	0.901
Machchobinskoye	1.394	0.896
Nelbinskoye	1.392	0.895
Verkhnevilyuchanskoye	1.363	0.882
Irelyakhskoye	1.386	0.892

the component composition of natural gas, from which it has been synthesized (Table 1).

Molar mass of hydrate (Table 2) was calculated from the equation: $M_h = M + 6 \cdot 18$, where $M = \Sigma N_i M_i$ (N_i is the molar fraction of i-th component of natural gas; M_i is the molar mass of i-th component of natural gas).

Packing degree for small and large bags of hydrate with hydrate-forming components in structures I and II depends on the partial pressure of i-th component in the gas phase and it can be calculated with the use of Langmuir constants C_i (in Pa^{-1}) [4]:

$$C_i = \frac{A_i}{T} \exp \frac{B_i}{T} \quad (4)$$

where A_i and B_i are constants that depend on the properties of hydrate-forming molecules [4]; T is the hydrate formation temperature, K.

Table 3 gives the results of calculation of packing degree for small and large bags in hydrate by individual hydrate-forming components by the equations

$$\theta_{i\,s/b} = \frac{C_{is/b} P_i}{1 + \sum C_{i\,s/b} P_i} \quad (5)$$

$$\theta_{i\,l/b} = \frac{C_{il/b} P_i}{1 + \sum C_{i\,l/b} P_i} \quad (6)$$

It is evident that both small and large bags are filled in each of the formed hydrates. It is common knowledge that packing degree for hollows may vary within the limits of 0–1. Hydrates are thermodynamically stable only in the case that at least one of the two types of bags is full by $\theta \geq 0.95$ [5]. Since packing degree for small and big bags is more than 0.95, both cubical structures are steady under the given synthesis conditions of hydrates.

TABLE 5

Volume of natural gas in hydrate as a function of its structure, m^3/L

Fields	Structure I	Structure II
Srednebotuobinskoye	0.248	0.159
Taas-Yuryakhskoye	0.247	0.159
Botuobinskoye	0.247	0.159
Machchobinskoye	0.248	0.159
Nelbinskoye	0.247	0.159
Verkhnevilyuchanskoye	0.252	0.159
Irelyakhskoye	0.247	0.159

Upon the calculation of bag packing degrees, the densities of the obtained hydrates were calculated from the equations (2) and (3).

From data of Table 4 it can be seen that the density of the synthesized hydrates of natural gases of the cubic structure I is 1.4 times more than the ice density, and the density of the cubic structure II is less than the ice density.

From data of Table 5 it can be seen that 1 L of solid hydrate in any one of the reviewed fields may contain from 160 to 250 L of natural gas. The values of gas volumes that have been obtained by way of calculation will be accurate under condition of the full passing of the whole water volume into gas hydrate phase and without taking into account the real processes that occur in the pore space of oil reservoir rock.

CONCLUSIONS

1. It has been found that natural gases of the reviewed fields of Yakutia form hydrates of a mixed structure, KS-I and KS-II.

2. Density of hydrates of the cubic structure I range from 0.882 to 0.901 g/mL, and that of hydrates of the cubic structure II, from 1.363 to 1.404 g/mL.

3. The volume of gas that is present in 1 L of solid hydrate may amount from 160 up 250 L, which is crucial for the viability to employ gas hydrates as an additional source of hydrocarbon raw.

REFERENCES

1 V. A. Solovyev, *Ross. Khim. Zh.*, XLVII (2003) 59.
2 Yu. F. Makogon, *Ibid.*, XLVII (2003) 70.
3 S. Sh. Byk, Yu. F. Makogon, V. I. Fomina, Gazovye gidraty, Khimiya, Moscow, 1980.
4 A. G. Groisman, Teplofizicheskiye svoystva gidratov, Nauka, Novosibirsk, 1985.
5 V. A. Istomin, V. G. Kvon, Preduprezhdeniye i likvidatsiya gazovykh gidratov v sistemakh dobychi gazov, PEC Gazprom, Moscow, 2004.