

# SPECIALTIES OF EXPLOITATION OF THE NATURAL GAS HYDRATE FIELDS IN PERMAFROST CONDITIONS

(Results of study gas hydrate formation and dissociation in a pore space)

*Yuri F. Makogon*

## Contents

Foreword . . . . .	1
Location of deposits containing natural gas in the hydrate state . . . . .	1
Determining the reserves of gas in the gas hydrate deposits	4
Several results of studying the conditions of hydrate formation and decomposition in porous medium . . . . .	6
Conclusions . . . . .	12
Literature references . . . . .	12

Moscow, 1966 VNIIEGAZPROM

(МОСКВА, 1966 ВНИИЭГАЗПРОМ)

*Introduction*

*The presented booklet considers the conditions of the natural gas hydrate formation in a porous rock. This work proposes a method for calculating the natural gas reserves in the deposits containing hydrates.*

*Also the conditions of gas hydrate decomposition in a porous rock are considered, and the principles of developing the natural gas hydrate deposits are recommended. The work is of the special interest with respect to the large perspective reserves of the natural gas in the permafrost zone and offshore with depth of water more than 500m.*

### **Location of deposits containing natural gas in the hydrate state**

Permafrost in the USSR is spread over the territories of Irkutsk, Magadan, Chita, Tomsk, Sverdlovsk areas, the Ukhta region of the Komi ASSR, the Khabarovsk and Krasnoyarsk regions, the Yakutia and Buriatia autonomous republics (1). It occupies the area of 10 millions of square kilometers ( $4 \times 10^6$  square miles) which is nearly 47% of the total area of the country.

Until the recent time it was thought that the permafrost layer is limited to the depth of 600-700 m. However, the existence of the permafrost rock at depths up to 1400 m. was proven by the drilling and testing of the thermal regime of the Markhinskaya well located in the North-West of Yakutia ASSR\*. At the depth of 1800 m the layer temperature in this well was 3.8 °C (see Figure 1).

---

\* According to the data from the Yakutsk Territorial Geological Department.

Tremendous reserves of oil and natural gas are situated in the permafrost regions. The perspective natural gas deposits were discovered in the Western and Eastern Siberia with the potential reserves over 10 trillion  $m^3$ . With respect to that the natural gas deposits may be located in the permafrost rock zones. Figure 2 presents the isotherms of the permafrost zones spreading (2) at various depths. The M-N line indicates the permafrost rock penetration depth.

Basing on the hydrostatic pressure distribution the curve AB reflects the equilibrium conditions of hydrate formation from natural gas of the density 0.6 relative to air. The zone bounded by this curve characterizes the magnitude of pressures and temperatures at which the natural gas in the deposit is in the hydrate state. Even in the area located above the 0°C isotherm the natural gases are in a hydrate state, and not in a free state in contact with ice, because the deposits of gas were formed much earlier than the permafrost penetrated into the deep layers of rock.

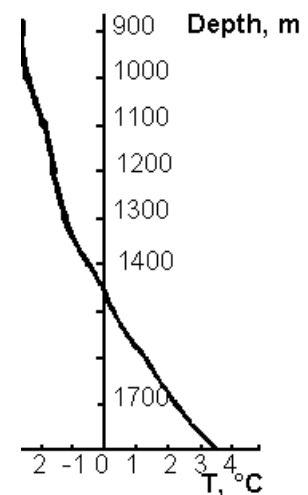


Figure 1. Thermogram of the Markhinskaya No. 1 well.

As the temperature in the layer decreases below 0°C the water in hydrate does not transform into ice.

The southern boundary of the permafrost zone is shown on the map of the USSR (Figure 3). This picture also presents the possible locations of the fields in which the natural gas is in the hydrate state. This zone is bounded by the 0°C isotherm at the depth of 100 m, where it corresponds to the equilibrium temperature of hydrate formation from the natural gas of the density 0.6 relative to air and the layer pressure of 10 atm (corresponding to the hydrostatic pressure).

\* The method of flipping the heterogeneous gas hydrate equilibrium diagram was used in constructing this plot. Layer pressure was taken as the hydrostatic. Equilibrium P-T conditions of hydrate formation were the function of the composition of water and gas.

Below the 0°C isotherm the hydrates of natural gases form in the layer, and the boundary of their location is defined by the curve AB (Figure 2). During the geophysical logging of deposits it is necessary to consider that gas in the hydrate formation zone is present completely or partly in a clathrate (solid) state.

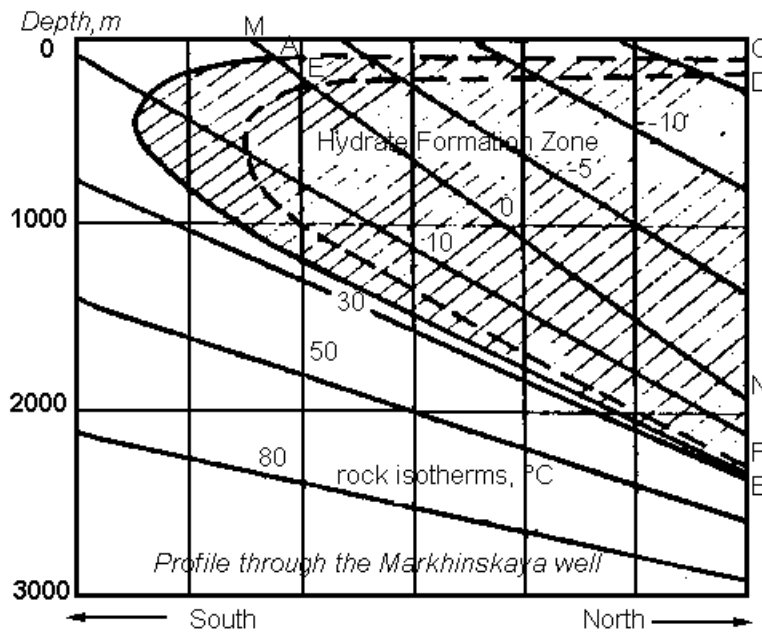
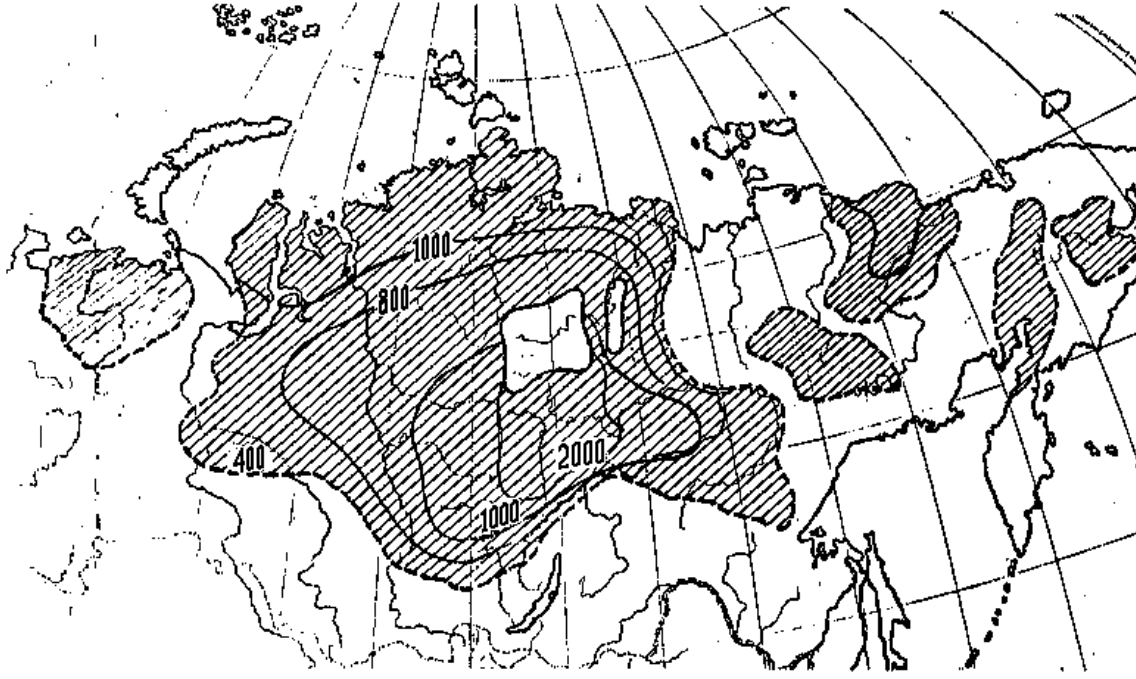


Figure 2. Diagram of the hydrate formation zone distribution in the presence of permafrost.\*

## Determining the reserves of gas in the gas hydrate deposits located in permafrost zones

Gas may be present in a free or in a hydrate state in the gas hydrate field. The ratio is determined by the various factors: porosity, amount of the water tied up in the porous



**Figure 3.** Schematic map of the potential hydrate formation zones ( $H > 400$  m). space, the composition of gas, presence of the gas migration during the formation of hydrates in the deposit, etc.

During the formation of hydrates in the layer, part of the gas transforms into a hydrate, and if the gas-water interface is mobile, volume of the deposit decreases significantly, because during the hydrate formation  $1 \text{ m}^3$  of the pore water can tie up from  $71.1$  to  $215.7 \text{ m}^3$  of gas. If the initial gas-water interface is fixed, then the hydrate formation is accompanied by the decrease in the layer pressure. The natural gas hydrate deposits with the anomalously low pressure can be found when the immobile gas-water interface exists. During the well drilling in such structures a high consumption of the drilling mud is possible. Decrease of the deposit volume or of the gas pressure must be considered during the estimation of the reserves of natural fuel in the gas hydrate deposit, since the reserves may be much larger that the predictions from the data on the deposit volume and pressure.

Reserves in the deposits containing gas totally or partially in a hydrate state are calculated using the equation

$$Q_G = V_G \cdot m_E^H \frac{P_L \cdot 273}{ZT} + V_G m S_R \psi \quad (1)$$

where

- $V_G$  - volume of the deposit after its transition into a hydrate state,  $m^3$ ;  
 $m_E^H$  - the effective layer porosity with gas present in a hydrate state;  
 $m$  - the total porosity, fraction of 1;  
 $S_R$  - volume of the water reacted (transformed into hydrate);  
 $P_L$  - pressure in the layer, atm;  
 $Z$  - gas compressibility in the deposit conditions;  
 $T$  - deposit temperature, K;  
 $\psi$  - reactivity coefficient equal to the number of the volumes of gas (at normal conditions) contained in one volume of water during their transition into a hydrate state,  $m^3/m^3$ :

$$\psi = \frac{22.4 \cdot 1000}{M_G} \quad (2)$$

where

- $M_G$  - molar mass of the gas (for  $CH_4$ ,  $M_G^{C_1} = 124$ ; for  $C_2H_6$ ,  $M_G^{C_2} = 160$ ; for  $C_3H_8$ ,  $M_G^{C_3} = 350$ ; for  $C_4H_{10}$ ,  $M_G^{C_4} = 364$ ).

If, during the formation of hydrate, in the layer or after the deposit transformation into a hydrate state there is no migration of gas, then a part of gas will be in a free state. The volume of a free gas in this case is calculated using the equation

$$Q_G^{free} = V_G \cdot m_E^H \frac{P_L \cdot 273}{ZT} \quad , m^3 \quad (3),$$

and the volume of gas tied up with water with the formula

$$Q_G^{solid} = V_G m S_R \psi \quad , m^3 \quad (4).$$

The amount of gas in the deposit after the hydrate formation remains constant (part of the gas is in the free, and part in the solid state), but the volume of the deposit, as it was said before, at  $P_L \approx \text{const}$ , changes significantly, which can be calculated using the following expression:

$$\eta = \frac{V_G m}{V_0 m} = 100 \frac{(1 - S_w) \frac{P_L \cdot 273}{ZT} + S_w \lambda}{m_E^H \frac{P_L \cdot 273}{ZT} + S_R \psi} \% \quad (5)$$

where

- $\lambda$  - solubility of gas in water at the layer conditions,  $m^3/m^3$ ;  
 $V_0$  - volume of deposit prior to its transition into a hydrate state,  $m^3$ ;  
 $S_w$  - content of the tied-up water in the pores, fraction of the pore volume.

Deposits of the equal volumes with the gas in a hydrate and a free states at the same layer pressure contain different amounts of fuel. There is more fuel in the deposit located in the hydrate formation zone. This differences found from the equation

$$N = \frac{Q_G}{Q_0} = 100 \frac{m_E^H \frac{P_L \cdot 273}{ZT} + S_R \psi}{(1 - S_W) \frac{P_L \cdot 273}{ZT} + S_W \lambda} \% \quad (6)$$

i.e. the larger are the coefficients  $S_R$  and  $\psi$ , the larger gas reserves are in the hydrate deposit, compared to the regular one.

### Several results of studying the conditions of hydrate formation and decomposition in porous medium

With the purpose of determining the conditions of hydrate formation and decomposition in the porous medium, a set of experiments was performed in the dedicated gas laboratory of the Moscow Oil and Gas Institute. Several results are presented below.

The study was done using the natural gas of the composition indicated in Table 1. This table also presents the characteristic change in the composition of gas during the formation and decomposition of hydrate.

Table 1. Change of the initial gas composition during the hydrate formation and decomposition.

Natural gas	Components, %					
	N <sub>2</sub>	CH <sub>4</sub> +N <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	i-C <sub>4</sub> H <sub>10</sub>	n-C <sub>4</sub> H <sub>10</sub>
Initial gas	1.3	93.4	5.05	1.27	0.14	0.1
Gas above hydrate	3.3	96.28	3.6	0.12	-	-
Gas after hydrate decomposition	0.3	79.2	13.5	6.2	0.8	0.3

The experiments were performed in four thermostatic cells of the volumes ranging from 360 to 980 cm<sup>3</sup> filled with the porous medium - quartz sand pressurized to 270 atm. The grain size analysis of the sand for the two series of experiments is presented in Figure 4.

The densified porous medium was saturated with water, and then a part of water was displaced by gas. The amount of the tied-up water ranged from 30 to 75 % of the total porosity. The effective porosity was 12 - 22 %.

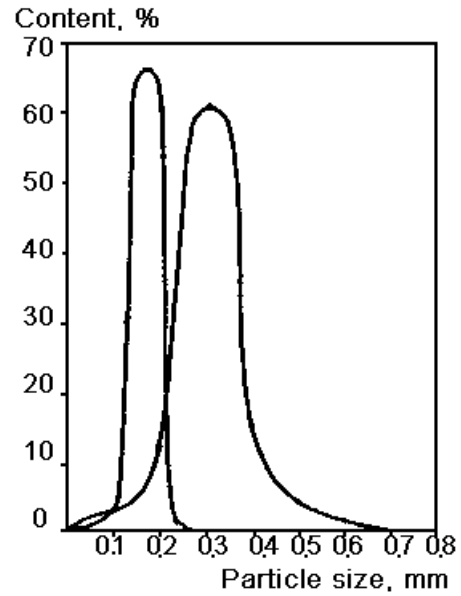
The pressure was measured using the sample manometers, the temperature - by the alcohol-based thermometers and thermocouples inserted in the porous medium.

Formation and decomposition of hydrates in the porous medium was determined through the control of the gas composition, the temperature and pressure in the cell with the known effective volume of the porous space and the volume of gas, and also through the volumetric method. One of the characteristic curves of the pressure drop (ABD) during the lowering of temperature and hydrate formation in the porous medium is presented in Figure 5. This figure also presents the calculated curve of decreasing pressure and temperature in the cell without hydrate formation (curve ABC). The point B at the intersection of the curves ABC and ABD corresponds to the conditions (pressure and temperature) of the onset of hydrate formation. The curve EFG indicates the lowering of temperature, point G corresponding to the temperature of the onset of hydrate formation at the pressure analogous to the point B.

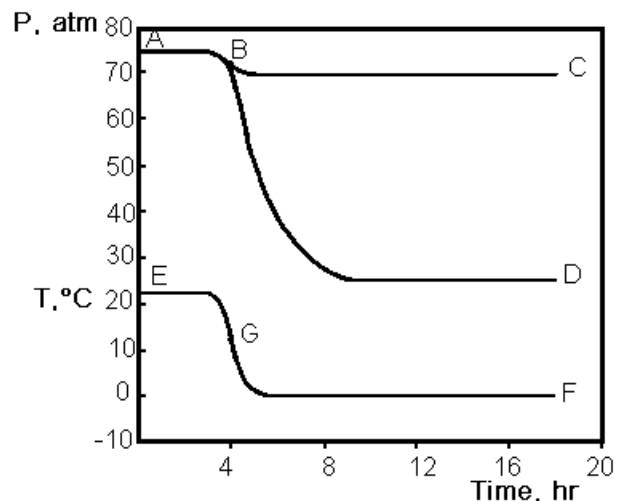
From the experimental results a diagram was constructed (Figure 6) where the curve 1 indicates the formation of hydrate from gas contacting the free water surface, the curve 2 -in contact with the pore water.

Hydrate formation in such conditions proceeds differently. The temperature in the first case (curve 1) is lower by 2 - 5 °C, and the energy is higher than in the second case (curve 2), which is caused by the interaction of the pore water with the layer.

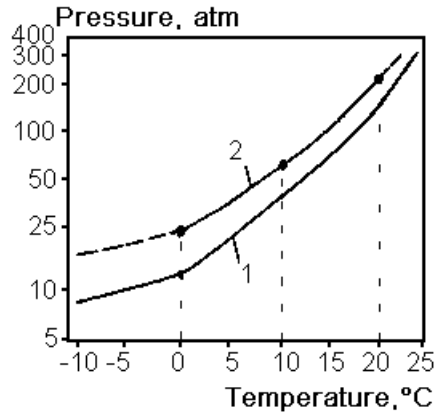
The smaller is the pore size and the thinner is the film of water and the lower is the radius of the pore water



**Figure 4. Sizes of the quartz sand grains of the porous rock.**



**Figure 5. Change of pressure during the hydrate formation in porous medium.**



**Figure 6. Conditions of the natural gas hydrate formation at the free water surface (1) and pore water (2).**

surface curvature, the higher is the hydrate formation pressure at the fixed temperature.

From the obtained data the curve DEF was constructed (see Figure 2), bounding the zone of potential hydrate formation in the conditions close to those studied. Experiments were performed with the constant initial mass of gas in the cell of a fixed volume. Such conditions are characteristic to the natural gas deposits with the immobile gas-water contact.

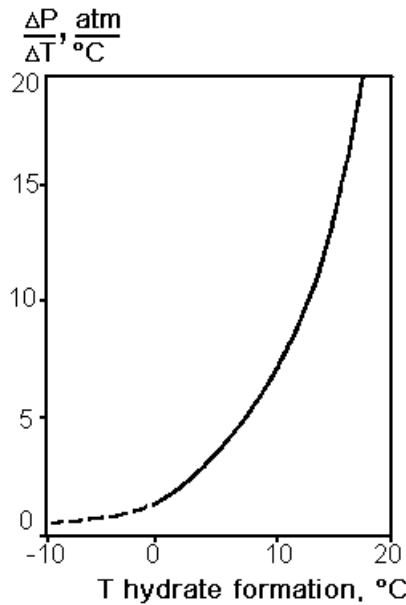
Lowering of the pressure in the closed deposit with respect to the initial pressure during hydrate formation is determined from the formula

$$P_H = \frac{P_0(1-S_w) \frac{273}{ZT} - S_w \psi}{m_E^H \frac{273}{ZT}}, \text{ atm} \quad (7)$$

where

$P_0$  - initial pressure before the hydrate formation;

$P_H$  - deposit pressure after the hydrate formation.



**Figure 7. Curve of the  $\Delta P/\Delta T$  dependence as the function of temperature of the hydrate formation process.**

Besides that, the studies were performed with the fixed initial pressure. Such conditions are analogous to those in the deposits with the moving gas-water interface.

The pressure in the layer then remains constant, and the volume of deposit decreases. This decrease compared to the initial volume is determined by the equation (5).

Let us consider the two characteristic examples of hydrate formation in porous medium.

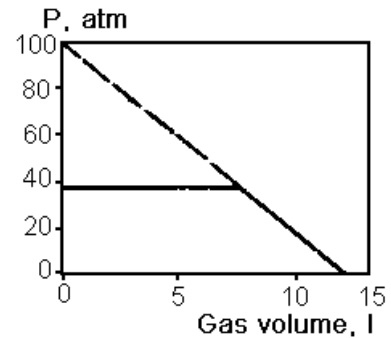
1. Hydrate formation in a fixed volume cell, i.e. without additional gas supply, when the pressure decreases to the equilibrium value corresponding to the cell temperature. For example, the initial pressure of 100 atm with lowering the temperature from 20 °C to 5 °C decreases to 37 atm.

Hydrate formation occurs at 14 °C. At the initial pressure of 70 atm the hydrate starts to form at 11 °C (curve 2 on Figure 6) and with lowering the cell temperature to 0 °C the pressure in the cell decreases to 25 atm.

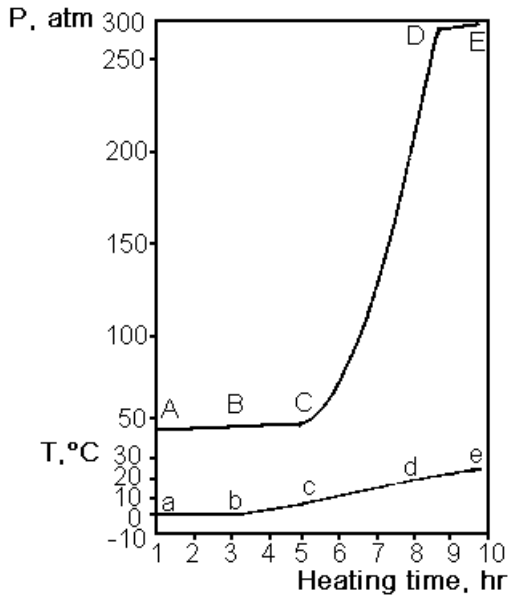
Figure 7 presents the dependence of the pressure decrease in the cell ( $\Delta P$ ) as the function of lowering the hydrate formation temperature ( $\Delta T$ ). The higher is the initial temperature of the onset of hydrate formation, the larger is the pressure drop with lowering the temperature by one degree, i.e. with lowering the temperature and pressure the intensity of hydrate formation decreases.

The change of pressure during the venting of gas from the cell, where a part of gas is in the hydrate state, is graphed in Figure 8. If there is about 12.3 liters of gas in the cell with a porous medium saturated with water in the free pores volume equal to 0.1 l with  $P = 100$  atm and  $T = 20$  °C, then during the hydrate formation ( $T = 5$  °C) this amount of gas is contained in a cell at the pressure of 37 atm (point A, Figure 8). In other words at a fixed pressure the volume of gas in the cell filled with hydrate is approximately three times larger than in the cell without hydrate. The point D in Figure 8 corresponds to the initial pressure in the cell containing the same 12.3 l of gas in a free state without the hydrate.

When the gas is vented from the cell without hydrate the pressure decrease follows the line DBC (Figure 8), and in the presence of hydrate during the initial period of gas venting the pressure is constant (AB), equal to the hydrate decomposition pressure.



**Figure 8. Pressure change during the gas venting from the cell containing a part of gas as hydrate.**



**Figure 10. Pressure change during the hydrate decomposition in porous medium of the cell with the temperature increase.**

temperature. If the venting rate is higher than the rate of gas accumulation, then the cell pressure follows the curve ABD. The volume of gas contained in the cell without hydrate at  $P = 55$  atm is 12 l (point G), pressure during gas venting from such a cell follows the line AG. However, in the presence of hydrate in the cell (at  $T = 0$  °C) lowering the pressure to 25 atm results in hydrate decomposition and pressure stabilization (line BC) until their complete decomposition, after which the pressure decreases along the line CD. If the temperature of 5 °C is maintained in the cell, the pressure during hydrate decomposition is 37 atm, and the pressure decreases along the line AEFD.

The volume of gas in the cell with hydrate was equal to 41 l, i.e. the gas “reserve” increase from the equation (6) is

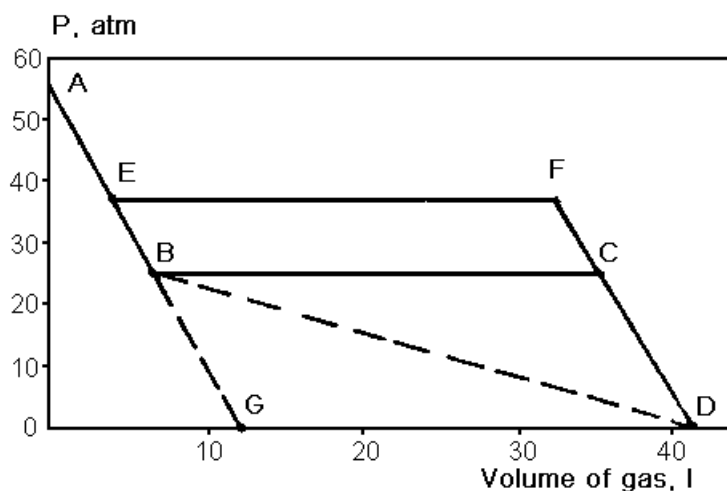
$$N = \frac{Q_G}{Q_0} = \frac{41}{12} = 3.41$$

In other words, the reserve of gas in the hydrate

After the complete decomposition of hydrate (point B) the further venting of gas is accompanied by the pressure drop (BC).

2. If the constant pressure is maintained, then during the hydrate formation gas is accumulated in the cell. The volume of the accumulated gas may exceed by several times the volume of gas corresponding to the pressure and temperature in the cell without hydrate. Then the amount of gas in the cell (layer) is determined by the equation (1). For example, at the constant pressure of 55 atm and  $T = 0$  °C gas hydrate forms in the cell. A part of gas is in the free state, and the other part is in the hydrate state.

Figure 9 presents the dependence of pressure on the different conditions of gas venting from the cell. When a gas is vented from the cell at  $T = 0$  °C, the pressure decreases (curve ABCD) is the venting rate does not exceed the rate of gas accumulation from hydrate decomposition at the specified



**Figure 9. Pressure change in the cell with the venting of gas during the hydrate decomposition at the constant temperature.**

deposit is 341 % higher than in the regular deposit at the same conditions.

Decomposition of hydrate in the porous medium was performed through lowering the pressure and increasing the temperature. During the temperature increase of the porous medium in a closed cell above the equilibrium value hydrates decompose and the pressure increases to its initial value. If hydrates in the porous medium form at a constant initial pressure, then their decomposition through the temperature increase results in a significant increase of pressure which can be calculated using the equation:

$$P_K = \frac{m_E^H \frac{P_H \cdot 273}{ZT} + S_w \psi}{(1 - S_w) \frac{273}{ZT}}, \text{ atm} \quad (8)$$

where

$P_H$  - the hydrate decomposition pressure.

Thus, for example during the hydrate formation in the cell with the constant pressure of 50 atm and constant temperature of 2 °C, rising the temperature to 24 °C resulted in a pressure increase to 270 atm (Figure 10).

It is worth noting that in the closed deposit with the initial hydrostatic pressure of 50 atm (the rock pressure is about 125 atm) the hydrate decomposition through the sharp increase in temperature can result in an excessive increase of pressure in the layer and “explosion” of the deposit. That is why the heating of the field with the purpose of hydrate decomposition must be carried out in a way that the gas pressure does not exceed the rock pressure.

Along with the heating and depressurizing in order to produce gas from a hydrate deposit one can use the injection of inhibitors( alcohols, glycols, electrolytes, etc.) into the layer which decompose hydrates.

## Conclusions

1. Natural gas can exist in the permafrost regions partially or completely in a hydrate state in the layer conditions.
2. Depth of the gas hydrate deposit location depends on the depth of permafrost spreading, on the geothermal gradient below the permafrost layer, pressure and composition of water and gas, and also on the quality of the porous medium.
3. Reserves of gas in the gas hydrate deposits are significantly larger than in the non-hydrate deposits. The method of calculating the gas reserves in deposits containing gas partially or completely in a hydrate state is recommended.
4. During the uncovering of the “plugged”\* hydrate deposits an anomalously low layer pressure may exist, several times lower than the initial hydrostatic pressure.
5. Development of the deposits containing gas partially in a hydrate state can be performed by lowering the pressure corresponding to the hydrate decomposition

conditions, by heating of the deposit above the hydrate decomposition temperature, and by injecting inhibitors in the layer.

6. With the apparent water flooding regime the heating method must be used, because lowering of the pressure will result in water entering the layer and covering the gas in hydrates.

7. During the hydrate fields development there exists a period of the constant layer pressure when the gas production at the equilibrium pressure is accompanied by the decomposition of hydrate. The higher is the deposit temperature, the higher is the surface of the constant pressure.

8. During the hydrate formation at the constant pressure a large accumulation of gas occurs, which can produce pressures in the fixed volume during decomposition much higher than the initial pressure.

### Literature references

1. Osnovy Geokriologii (Merzlotovedeniya) (General geocryology), part 1, Akademiya Nauk SSSR, 1959.
2. Makogon, Y. F., Hydrate Formation in the Gas-Bearing Layer in Permafrost Conditions., Gazovaya Promyshlennost (Gas Industry), 1965, No. 5.

### СОДЕРЖАНИЕ

Размещение залежей, содержащей природный газ в пласте в виде гидратов .....	3
Определение запасов газа в залежах, покрываемых в зонах вечной мерзлоты .....	5
Некоторые результаты исследования условий образования и разложения гидратов в пористой среде .....	8
Выводы .....	15
Литература .....	17

### ГАЗОВАЯ ПРОМЫШЛЕННОСТЬ № 8

Юрий Федорович Макогон

### ОСОБЕННОСТИ ЭКСПЛУАТАЦИИ МЕСТОРОЖДЕНИЙ ПРИРОДНЫХ ГАЗОВ В ЗОНЕ ВЕЧНОЙ МЕРЗЛОТЫ

Научный редактор К.С. Басин  
Редактор Э.Н. Исатаев  
Технический редактор В.А. Елизур  
Корректор А.А. Хорошева

Л-26775

Подписано в печать 11.7.1966 г.

Формат 84x108/32

Уч.-изд. л. 0,8

Печ. л. 0,8

Бум. л. 0,8

Тираж 1000

Заказ 256

Цена 4 коп.

Ретоврият ЦНТИ Магдаларома