

Experimental Study of Methane Hydrates in Coal

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Abstract. The possibility of gas hydrate formation in porous space of coal has been studied. The experiments conducted have proven the possibility of methane gas hydrate formation in moist coal. It has been demonstrated that the decomposition points of methane gas hydrates in coal are near to the phase equilibrium curve for bulk methane hydrate. Only part of water absorbed by coal can be involved in the methane gas hydrate formation. With the increase in gas pressure increases the amount of gas hydrate formed in natural coal. For formation of hydrates at a positive temperature, the pressure in the system has to be at least 2 MPa. At the same time the speed of formation and decomposition of gas hydrates in coal is big enough.

1 Introduction

In the process of metamorphism of coal matter about 300 m³ gaseous substances are formed per each ton of coal [1-4], generally they include carbon dioxide, methane, and nitrogen. The reservoir pressure of methane, on average, linearly depends on depth and for different coal seams it is in the range $(0.4 \div 1)\gamma H$, where γH is the rock pressure of undisturbed coal seam, $\gamma = 25\ 000\ \text{H/m}^3$ is the average specific weight of rocks, and H (m) is a seam depth from a daylight surface. Respectively, for the seams lying at a depth from 400 to 600 meters, gas pressure can reach 4÷15 MPa. In spite of the fact that coal bed methane is a valuable raw material for industrial use, in modern conditions of mining technology methane is frequently considered as an accessory and dangerous product of mining [4], especially in case of underground mining. In fact, almost all researchers [2-6], carrying out estimates of amount of the methane in a gaseous state absorbed on a surface and adsorbed in volume of solid substance, come to the conclusion that the actual content of methane in

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natural coals often surpasses their estimates. Therefore, it is necessary to look for other forms of methane location in coal mass. The assumption was made of a possibility of finding methane in a form of gas hydrates, which are formed from coal bed methane and natural moisture under suitable pressure-temperature conditions [7-9]. Gas hydrates are clathrate compounds in which molecules of gas-hydrating agent are included in cavities of the polyhedral framework constructed of water molecules. One volume of methane hydrate can contain about 170 volumes of gas [10-14]. The lowest homologues of hydrocarbons (C1-C4), carbon dioxide, nitrogen, oxygen, etc. can act as a hydrating agent. The existence of hydrates needs increased pressure and, as a rule, below room temperature. In most cases temperature of decomposition of hydrates increases with growth of pressure. So, equilibrium pressures of hydrate of pure methane at 0 and 10 °C are up to 2.51 and 6.95 MPa respectively [10]. In this paper the results of pilot studies of formation and decomposition of methane hydrate in pore space of natural coal are presented. The main objective of research was to define pressure-temperature conditions under which the formation and decomposition of gas hydrates in pore space of natural coal occurs, and also to find out amount of water, capable of being involved in the formation of gas hydrates.

2 Experimental unit

The basic component of the used experimental unit is the cylindrical high pressure autoclave made of stainless steel and furnished with the gate valve, the pressure transformer and the thermocouple incorporated inside. The autoclave is located in the programmable cryostat. Before the experiment, the coal sample is loaded into the autoclave, free volume is washed out by methane several times for removal of air and the working pressure of gas is created. For experiments pure methane and carbon dioxide were used. In both cases the amount of impurity in each of these gases was less than 0.01%. The thermocouple is installed in the geometric centre of the cylindrical autoclave. Gas pressure in the autoclave, temperature inside the autoclave, and also temperature of the thermal liquid washing the autoclave outside are measured by means of the pressure transducer and temperature transducers. Data from the transducers are registered every 20 seconds by the computer.

Before loading in the autoclave, the coal preparation had been carried out. The selected natural coal was dried up in the vacuum furnace at a temperature of 110 °C within 4 hours till complete loss of moisture. Then the sample of coal was located in a desiccator with the constant air humidity, its humidity was measured in accordance with the change of mass of coal. To maintain the constant humidity in the desiccator, a Petri dish with the distilled water or saturated salt solution was put inside. Within several days (5 and more) the mass of coal reached the constant value, the equilibrium humidity of coal without contact with liquid water was reached. The sizes of particles of the coal taken for experiments were in range from 0.5 to 2.0 mm.

3 Results of the experiments and discussion

3.1 Isotherms of water sorption by coal sample

The formation of gas hydrates in porous space of coal depends on the form and the amount of moisture present in coal. Before carrying out experiments the water sorption isotherm of the K grade coal sample taken from outburst-prone seam XXVII of mine "Berezovskaya" in Kemerovo district was studied. Dependence of the established humidity of coal on relative air humidity in which the coal was kept is given in fig. 1 – the sorption isotherm at 22 °C. By its form the received curve is similar to those found in literature [16-18].

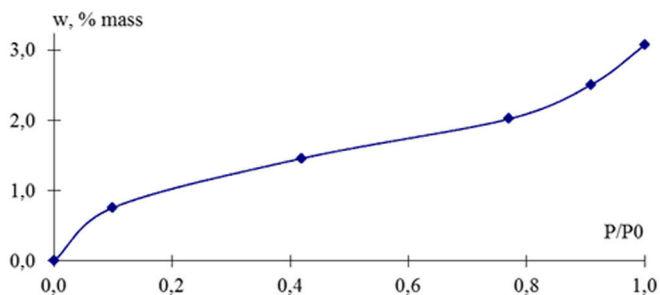


Fig. 1. Water sorption isotherms of K grade coal at temperature 295K.

3.2 Experiments on formation and decomposition of gas hydrates in coal

For carrying out experiments the prepared coal of the known humidity was located in the autoclave in which the working pressure of gas was created. On the programmable thermostat the program of linear decrease of temperature was set to study formation of gas hydrates when cooling. To study the decomposition of gas hydrates, the program of linear temperature increase was set on the thermostat. In the absence of phase transformations, the linear change of temperature led to linear change of pressure in the autoclave. During the formation and decomposition of gas hydrates the step on a pressure curve occurred. Experimental data allowed calculating the volume of the methane in a gaseous state and therefore the amount of the methane involved in the formation of gas hydrates. On the basis of the amount of the methane participating in hydrate formation and the formula of hydrate $\text{CH}_4 \cdot 6\text{H}_2\text{O}$ it is possible to calculate percent of the moisture W_g participating in hydrate formation. The P-T chart of change of pressure and temperature in the autoclave containing gas and moisture coal in the course of the experiment under code 208 is given in Fig. 2. Gas emission peaks are clearly visible: positive peak when heating and negative peak when cooling of system. The arrows indicate the direction of the temperature change.

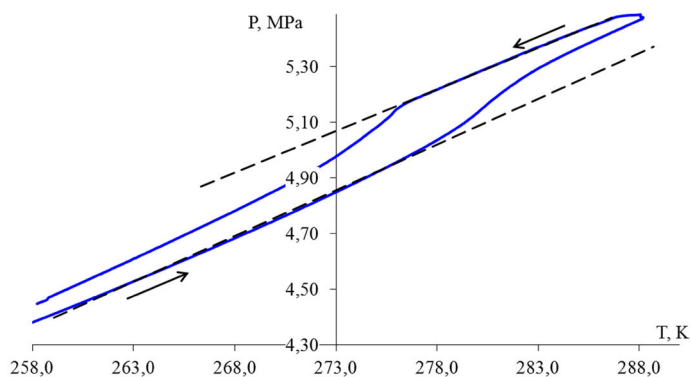


Fig. 2. P-T chart for experiment 208

To detect the trends of formation and decomposition of gas hydrates in natural coal a series of experiments was conducted. Usually (except 207, 208) experiments began at a temperature of +20 °C, then a linear decrease of temperature to -25 °C occurred, the hold for 60 minutes and again linear temperature increase with a constant speed. Decrease speed θ_1 and increase speed θ_2 temperatures for each experiment, and also pressure and temperature of the centre of the bend arising at formation and decomposition of gas

hydrates are specified in Table 1. In Table 1 the humidity of the coal W0 loaded into the autoclave, and also Wg – the amount of water which is involved in formation of gas hydrates converted into percent from the mass of coal is specified.

Table 1. Experimental points of formation and decomposition of gas hydrates, and amount of water involved in the formation of gas hydrates

Code	w ₀ , % mass	Formation upon cooling				Decomposition upon heating			
		Θ_1 , mK/s	P, MPa	T, K	Wg, %	Θ_2 , mK/s	P, MPa	T, K	Wg, %
207	2.67	-	-	-	-	5.56	5.07	280.1	0.97
208	2.67	5.56	5.14	275.9	0.79	5.56	5.13	279.8	0.67
625	2.81	2.22	4.48	272.7	0.71	1.04	3.78	275.5	0.84
627	2.81	6.25	2.38	271.9	0.47	1.11	2.16	268.4	0.69
629	2.81	6.25	5.30	276.6	0.84	2.08	5.27	278.4	0.93
709	2.95	2.08	4.16	273.2	0.57	0.83	4.17	276.9	0.86
711	2.95	6.25	2.31	268.5	0.60	2.50	2.33	269.4	0.69
716	2.42	4.17	5.34	271.4	0.42	1.04	5.54	278.9	0.67
717	2.42	-	-	-	-	2.50	2.46	269.5	0.43

In Figure 3 the experimental points of decomposition and formation of gas hydrates in natural coal are given. The zone of stable existence of methane hydrates is above and more to the left of the phase equilibrium curve drawn as a continuous line. As the moment of phase transition the centre of the bent has been accepted, i.e. the section with the biggest inclination on P-T chart. Taking into account the extent of phase transition it is possible to say that all points of decomposition lie near the phase equilibrium curve of methane hydrate. The formation of gas hydrates happens when the system cools down on 3÷5 K in reference to the equilibrium curve of phase transition. The received results can be explained by the influence of porous structure of coal and they can be compared to the data obtained by other researchers [19].

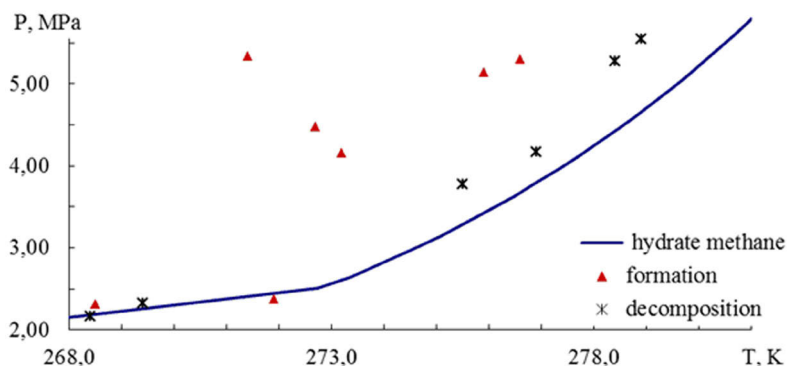


Fig. 3. The experimental points of decomposition of hydrates in natural coal.

The analysis of experimental data (Table 1) has shown that the amount of the moisture involved in hydrate formation is influenced by pressure of methane and humidity of coal. For construction of graphs in Fig. 4 and Fig. 5 the implemented experiments were arranged according to values of close humidity and close gas pressure. It can be seen that for each group of experiments with increase in the humidity of coal the amount of water, capable to be involved in hydrate formation monotonously increases. On the basis of the type of

dependence, it is possible to assume that for pressure of 2.2÷2.5 MP the moisture participating in hydrate formation exceeds a threshold in 1.7%, and for pressure of 5÷6 MP this threshold is 1.3% of absorbed moisture, it decreases at increase of gas pressure. This size of humidity (about 1.5%) approximately corresponds to plateau level on a sorption isotherm of water (Fig. 1).

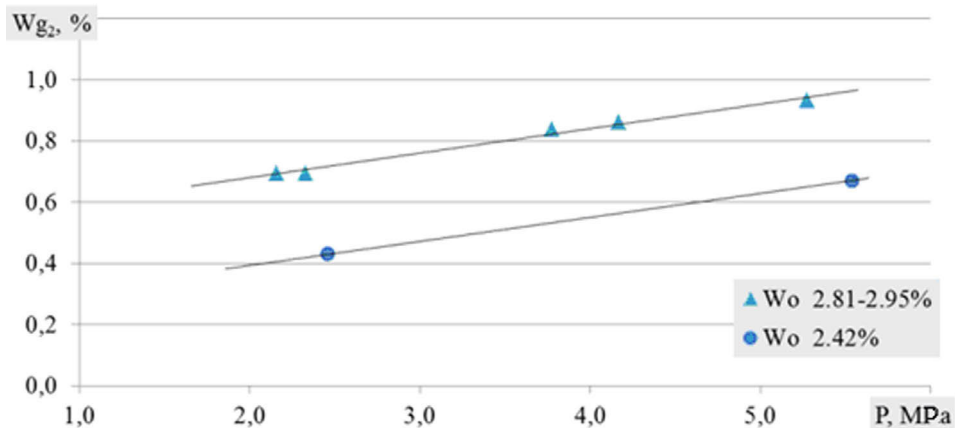


Fig. 4. The dependence of moisture involved in hydrate formation W_g on pressure of methane.

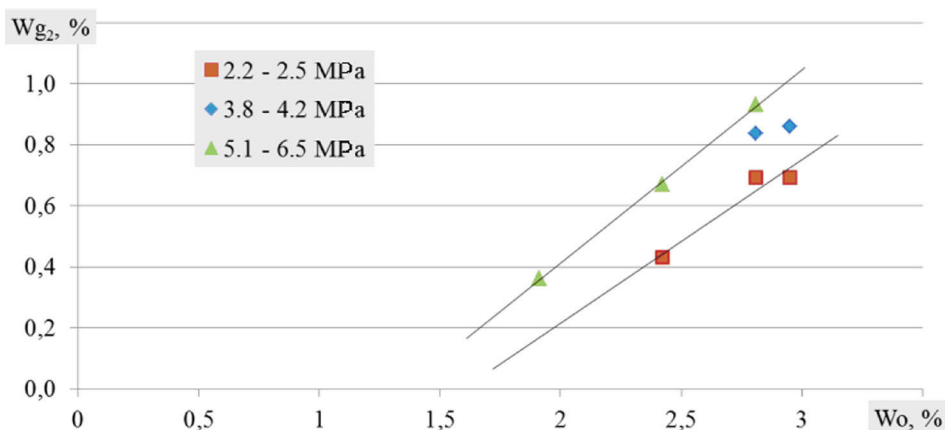


Fig. 5. The dependence of moisture involving in hydrate formation W_g on total moisture of coal W_o

4 Conclusions

Experiments show that in porous structure of natural coal, at the humidity corresponding to the term "air - dried coal" and suitable pressure and temperature, methane hydrates can be formed. Pressure and temperature conditions of formation and decomposition of methane hydrates in coal are close to the phase equilibrium curve. The amount of water involved in formation of gas hydrates always is less than humidity of coal. With increase in pressure of methane the amount of the hydrate formed in the taken coal sample increases. For formation of hydrates at a positive temperature, the pressure in the system has to be not less than 2 MPa. At the same time, the speed of formation and decomposition of gas hydrates in coal is big enough.

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