Problem of Pulverized Coal Formation at Mine Outburst Caused by Decomposition of Gas Hydrates in Coal Seams

V. G. SMIRNOV[1], V. V. DYRDIN[1], A. YU. MANAKOV[2], Z. R. ISMAGILOV[1,3] and T. P. ADAMOVA[2]

[1]*T. F. Gorbachev Kuzbass State Technical University,*
Kemerovo, Russia

E-mail: smirnovvg@mail.ru

[2]*Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,*
Novosibirsk, Russia

[3]*Institute of Coal Chemistry and Material Science, Federal Research Center of Coal and Coal Chemistry,*
Siberian Branch, Russian Academy of Sciences, Kemerovo, Russia

Abstract

The decomposition of methane hydrates in coal seams can be one of the causes of the origination of sudden emissions of coal and gas (coal outburst). The formation possibility of methane hydrate in the inner space of natural coal of several types was experimentally studied in the work. Experimental $P-T$ diagrams for a closed system containing wet coal and free methane, demonstrate the peak methane emission into the gas phase when intersecting the curve of the equilibrium of gas hydrates. Less than half of water, sorbed by coal is involved in the formation of gas hydrates. It was shown for the first time that with the degree decrease of metamorphism of coal, the amount of water that is absorbed by natural coal is increased, however herewith; a proportion of water involved in the formation of methane hydrate is decreased.

Key words: coal, methane, hydrates, sorption, desorption, $P-T$ diagram, sudden emissions of coal and gas

INTRODUCTION

At the underground bituminous coal extraction, the equilibrium state of a complex system containing solid, liquid, gaseous components and being for a long time under the impact of the mechanical rock pressure is disturbed. The disruption of equilibrium of a coal seam may be the cause of the emergence of dangerous gas-dynamic phenomena caused by the action of rock pressure and methane of coal seams [1–5]. Coal mines are a potential source of emissions into the atmosphere of methane, light hydrocarbon gases, polyaromatic compounds and fine coal dust.

Methane is a mandatory component of each coal deposit. Fossil bituminous coal is a natural hydrocarbon polymer, which was formed from vegetable deposits, in the aqueous, airless environment of ancient swamps covered in subsequent geological periods by the layers of sedimentary rocks and minerals [3, 6, 7]. At early stages of metamorphism from vegetable depositions, carbon dioxide and methane are evolved in approximately equal proportions, at the middle and late stages, methane and a small amount of other light hydrocarbon gases are formed. In the process of metamorphism on each ton of coal, up to 300 Nm^3 of methane is formed. For geological times, a part of methane is weathered from the coal seam, part remains. The registrable modern content of methane in coal seams can vary from units to several dozens of cubic meters on a ton of coal, and in some cases exceeds the value in 100 Nm^3 of methane on a ton of coal [3, 6, 7].

In a coal seam, methane can be present in the free condition (occupies the volume of open coal pores), be sorbed on the surface of coal pores and dissolve in the solid substance of coal [3−7]. The sorption capacity of coals is well studied, methods for measuring the free volume of coal pores were worked out [1, 7]. At the same time, the amount of methane liberated from coal often exceeds the sum of amounts of sorbed and free methane, at that, the allocation of methane from coal occurs irreversibly and only after taking off mechanic stresses. To explain the processes occurring at the release of methane gas from coal seams the theory suggesting the formation of solid gas-and-coal solutions (SGCS) is developed [8−14]. In particular, considering the amount of sorbed methane, as well as rates of the processes of sorption, diffusion and filtration, Oettinger [8, 9] makes the conclusion that these processes have characteristics of dissolution of methane in the solid substance of coal. Thus, methane sorption predominantly occurs in micropores of the coal substance, at the same time, the presence in the coal substance of methane and determines the formation of micropores in the process of coal metamorphism [8]. In the works [3, 10, 14], methane fractions, being in the free, sorbed and dissolved state, as well as gas-dynamic consequences of SGCS decomposition are assessed.

When developing coal seams coal and gas outbursts periodically occur, the formation mechanism of which cannot be considered completely studied. At an emission, the avalanche-like destruction of the edge zone of the coal seam and carry-over in the mined-out space of the coal mine of large quantities of coal, gas and small coal dust occurs. The amount of the simultaneously ejected coal is measured by hundreds or even thousands of tons, and the amount of ejected methane − dozens of thousands of cubic metres. Sudden outbursts of coal and gas often lead to the destruction of the mine equipment and overground constructions are the cause of fatal traumatizing of mining workers. A distinctive feature of each sudden outburst of coal and gas is the presence in the products of the outburst of micronized coal, called "explosive coal dust". About one third of the ejected coal turns into the "explosive coal dust" [1−5].
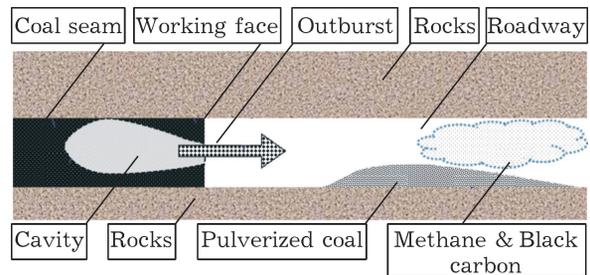

Fig. 1. Sudden outburst of coal and gas in a coal mine.

According to available data [1−6], the coal seams, in which there is a hazard of arising sudden outbursts of coal and gas, are characterized by a lowered mechanical strength and the presence of an interlayer of weak, broken coal (Fig. 1). Sudden outbursts of coal and gas most often occur near tectonic disorders intersecting the coal seam. The amount of methane ejecting at sudden outbursts of coal and gas often in two times exceeds the content of methane for the extracted mass of coal measured in the course of the normal development of a seam. A high content of methane and low mechanical strength of coal are necessary, but not sufficient conditions of the occurrence of sudden outburst that occur on not all seams that possess these features. It is quite possible that structure features of the specific coal and SGCS formed on its basis can influence the occurrence of sudden outburst of coal and gas.

The study of existence forms of methane in natural coals is a relevant scientific task. At the present time, the possibility of the existence of gas hydrates of methane in coal seams, as well as a probable influence of the decomposition methane hydrates on the occurrence of sudden outburst of coal and gas [15−19] are discussed. Gas hydrates are the compounds, in which molecules of non-polar or low-polarity gases are included in cages of the crystalline carcass built by water molecules [20]. Gas hydrates by the external appearance resemble ice; their many physical properties are close to properties of ice. About 170 of gas volumes are evolved from one volume of a gas hydrate when decomposing. Hydrates of natural gas are abundant in nature [20−22]. A necessary condition of the stable existence of gas hydrates is a high pressure, lowered temperature and

the availability of water, free hydrate-forming gas or sufficient concentration of hydrate-forming gas dissolved in water. For example, at a temperature of +5 °C for the stability of methane hydrate [22] a pressure above 4.3 M is required, and at a temperature of +9 °C − above 6.5 MPa. Carbon dioxide contained in coal seams is also capable of forming gas hydrates, moreover, under softer thermobaric conditions. At a temperature of +5 °C, for the stability of carbon dioxide hydrate, a pressure above 2.3 MPa is required, and at a temperature of +9 °C − above 4.5 MPa.

Earlier, we showed [17, 18, 23] that methane hydrate could form from inherent moisture, present in the pore space of natural coal of the type K selected from the outburst-prone coal seam No. XXVII, Berezovskaya mine. It was established that thermobaric conditions, at which the decomposition of this hydrate occurs, are close to the equilibrium curve of methane hydrate. Experiments [17, 18, 23] showed that only a part of water sorbed by coal is involved in the formation of gas hydrates. In the present work, the possibility of formation of gas hydrates in different types of coal is experimentally investigated.

EXPERIMENTAL SETUP AND PROCEDURE OF MEASUREMENTS

Experimental setup developed for the study of gas hydrates is shown in Fig. 2. The major element of the setup is a cylindrical autoclave made of stainless steel (2); equipped with a shutdown valve (3), pressure transducer (4), and thermocouple introduced inside (5). The autoclave is placed into a programmed cryostat (1). Before the experiment, a sample of coal is loaded into an autoclave, the free volume is washed with gas several times to remove air and operation pressure of a gas is created. Pure methane and carbon dioxide were used for the experiments. In the both cases, the amount of admixtures in each of these gases was less than 0.01 %. The thermocouple (5) is installed in the geometric centre of the cylindrical autoclave. Using transducers of pressure (4) and temperature (5, 6) the gas pressure inside the autoclave, temperature inside the autoclave, as well as the heat carrier temperature, circumambi-
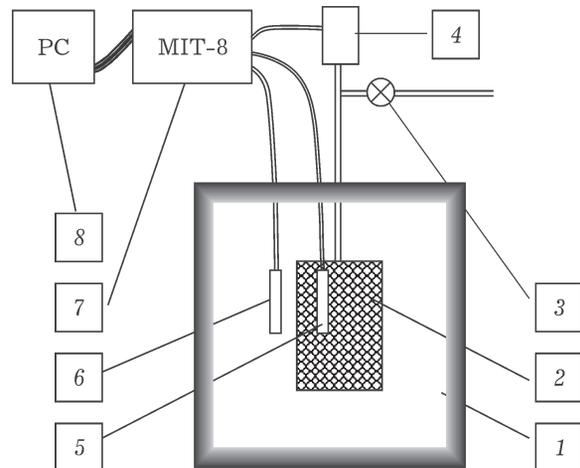

Fig. 2. Scheme of experimental setup: *1* − thermostat; *2* − autoclave with coal and gas; *3* − gas valve; *4* − pressure transducer; *5*, *6* − temperature transducers installed inside and outside the autoclave; *7* − multi-channel measure MIT-8; *8* − PC (personal computer).

ent the autoclave outside were measured. The data from the transducers are supplied to the measurer MIT-8 (multi-channel measurer temperature) (7) and once in 20 s is recorded by a computer (8).

Before loading the autoclave, the preparation of coal was conducted. Selected natural coal was dried for 4 h in a vacuum furnace at the temperature of 110 °C until the complete loss of moisture. Then, a sample of coal was placed into a desiccator with the constant air humidity; the humidity of coal was calculated on its mass change. To maintain the constant humidity a Petri dish with distilled water or a saturated saline solution was located in the desiccator. During several days (5 and more), the mass of coal reached the constant value, the equilibrium humidity of coal was achieved. It is noteworthy that the saturation by moisture occurred without the contact with liquid water, because of sorption of water vapours from the moist air. The particle coal sizes taken for the experiments were in the range of from 0.5 to 2.0 mm. It was shown in individual experiments that the amount of sorbed water (gram water/ gram coal) did not depend on the size of particles of coal. This suggests that water is sorbed precisely in the inner space of the coal substance.

To conduct experiments the prepared coal of the known humidity was placed into the

TABLE 1

Characteristics of coal samples used in experiments

Codes	Place of sampling: mine, seam	Type*	Maximal humidity, mass %	Ash content, mass %	Yield of volatile compounds, mass %	Combustion heat, MJ/kg
K	Pervomayskaya mine, seam XXIV	K	2.50	13.5−18.2	26−27	36.7
GZh	Uskovskaya mine, seam 50	GZh	4.35	9.1	39.1	−
1G	November 7th mine	G	4.71	17.5−20.7	44.5−46.0	24.3
2G	S. M. Kirov mine	G	9.77	27.6−31.2	42.0−43.0	19.8−21.6
D	A. D. Ruban mine, Polysaevskiy 2 seam	D	9.42	4.2	44	26.8

* According to Russian classification.

autoclave, in which the operation pressure was created in the range of 5−10 MPa, then the closed autoclave was stored in a freezer under thermobaric conditions of the stable existence of gas hydrates. In the course of the experiment, the closed autoclave at a low temperature was placed into a thermostat and after small ageing the program of a linear temperature increase was set on the thermostat. In the absence of phase transformations, this led to linear increase of pressure in the autoclave. If at the preliminary stage in the autoclave, gas hydrate was formed, then at exceeding the temperature above equilibrium for this hydrate its decompositions and, accordingly, gas evolution occurred. Due to this, a step arose in the curve of the pressure change. By the magnitude of the step, the amount of methane and water included in the formation of gas hydrates can be calculated, and the position of the step allows concluding about thermobaric conditions, at which the decomposition of the given hy-

TABLE 2

Results of the experiments conducted with coal samples of various types

Nos.	Coal	W_s, %	Gas	Experiment stages	W_h, %
1	K	2.26	CH_4	7.6 MPa +20 °C ↓ 6.1 MPa −10 °C (−4 °C/h)	0.50
				Ageing 1.5 h at −10 °C	
				6.1 MPa −10 °C ↑ 7.4 MPa +20 °C (+4 °C/h)	0.70
2	GZh	4.35	CH_4	8.4 MPa +20 °C ↓ 6.9 MPa −10 °C (−6 °C/h)	0.25
				Ageing 2.0 h at −10 °C	
				6.9 MPa −10 °C ↑ 8.2 MPa +20 °C (+4 °C/h)	0.50
3			CH_4	Ageing 650 h at −20 °C	
	1G	4.71		4.6 MPa −20 °C ↑ 6.0 MPa +20 °C (+6 °C/h)	0.64
4			CH_4	5.7 MPa +20 °C ↓ 4.6 MPa −15 °C (−6 °C/h)	no
				Ageing 150 h at −20 °C	
				4.4 MPa −10 °C ↑ 5.3 MPa + 20 °C (+6 °C/h)	0.52
5			CO_2	Ageing 40 h at −5 °C	
	2G	7.56		2.9 MPa −10 °C ↑ 4.1 MPa + 20 °C (+6 °C/h)	0.65
6			CH_4	Ageing 14 h at −10 °C	
				7.4 MPa −10 °C ↑ 9.2 MPa +25 °C (+6 °C/h)	0.20
7			CH_4	Ageing 40 h at −20 °C	no
	D	7.10		6.0 MPa −25 °C ↑ 8.2 MPa +25 °C (+6 °C/h)	
8			CH_4	Ageing 110 h at −20 °C	no
				5.0 MPa −20 °C ↑ 6.7 MPa +20 °C (+6 °C/h)	

Note. Experiment numbers are indicated; type of coal and humidity of samples (W_s, mass %); hydrate-forming gas; experiment stages; water quantity (W_h) involved in the formation of gas hydrates.

drate occurs. The free space of the autoclave at each load was calculated from the data on pressure drop in the autoclave caused by releasing the measured portions of the gas from the autoclave. In more details, the experimental technique and results obtained are described in the works [17, 18, 23].

RESULTS AND DISCUSSION

Types and characteristics of coal samples used for experiments are given in Table 1. The yield of volatile compounds is indicated in the calculation on the dry ashless state. The maximum humidity set out at ageing in a desiccator with a 100 % relative air humidity is indicated on the basis of our own measurements.

The information about the results and parameters of performed experiments are given in Table 2. The course of the experiment No. 2 is shown in Fig. 3 (see Table 2). In this experiment, coal GZh with the mass of 200.96 g, humidity of 4.35 %, free space inside the autoclave for the given load amounted to 141.2 mL was loaded into the autoclave. The pressure slightly above 8.5 MPa was created in the autoclave, after which it was kept at room temperature about 12 h until the end of the absorption processes of methane by coal. At such pressure and temperature, methane gas hydrate cannot form. The last hour and a half of ageing, the autoclave was located in a cryostat at the fixed temperature of +20 °C. In the cry-

ostat, a program of a linear temperature decrease to the value of −10 °C at the rate of 6 °C/h was set, then the autoclave was aged for an hour and a half at −10 °C for the formation of hydrate, after which the temperature of the heat-carrier in the cryostat was linearly increased to the temperature of +20 °C at the rate of 6 °C/h. The total duration of this experiment including cooling stages, ageing at a negative temperature, temperature increase amounted to 14 h.

In Fig. 3, curves *1* and *4* indicate $P-T$ curves characterizing the dependence of the measured gas pressure in the autoclave and temperature at the thermostat, and Figs. 2 and 3 indicate $P-T$ curves of the dependence of pressure on temperature measured in the geometric centre of the autoclave (curves *2* and *3*). Curves *1* and *2* describe the stage of decreasing the thermostat temperature, and curves *3* and *4* − the stage of the temperature increase. The gas pressure in all points of the autoclave is levelled out at once and has the same value near the walls and on the autoclave axis. At the same time, the temperature increase in the centre of the autoclave is behind the temperature increase of the heat-carrier because of a low heat conductivity of coal located in the autoclave. The horizontal distance between curves *1* and *2*, as well as between curves *3* and *4* corresponds to the coverage of temperatures, at which various portions of coal are located
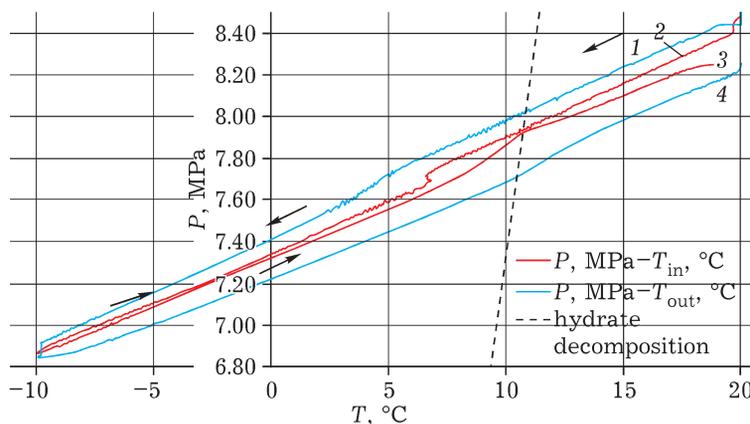

Fig. 3. Course of a typical experiment: *1* and *4* − pressure in the autoclave collated with the temperature of the heat-carrier; *2* and *3* − the same in the centre of the autoclave; curves *1* and *2* describe the stage of lowering the temperature and formation of gas hydrates; curves *3* and *4* − increase accompanied by their decomposition.

depending on their distance from the walls and axis of the autoclave (temperatures gradient in autoclave). Note that the change rate of the temperature of the heat-carrier was selected by the through trial and error method with the goal of reliable registration of the pressure drop value when decomposing a hydrate. The occurrence of temperature gradient inside the autoclave herewith was inevitable.

The heat effect of the phase transition (heat evolution at the hydrate formation and absorption at decomposition) also affects the inflection shape on curves *2* and *3* determining the dependence of the gas pressure from temperature measured in the centre of the autoclave. This leads to slowing down the temperature change inside the autoclave at a phase transition and more pronounced inflection on curves *2* and *3*, in comparison with curves *1* and *4*, respectively. The equilibrium curve of methane hydrate is depicted by a dashed curve. It can be noted that an inflection on the curve *4* starts at that moment, when thermobaric conditions in the near-wall region of the autoclave intersect the equilibrium curve, that is correspond to the hydrate decomposition located in the near-wall region. The hydrate located in the geometric centre of the autoclave is decomposed in the last turn, therefore, the ending of the inflection on the curve *3* correspond to the equilibrium conditions.

The list of the experiments on formation of gas hydrates in different coals is given in Table 2. In the column "experiment stages" the pressure and temperature at the start and end of the stage are indicated, symbol ↑ marks indicates the stage of increasing, and symbol ↓ indicates the stage of decreasing the temperature, the rate of the temperature change at the given stage is indicated in brackets. Between the stages of cooling and heating, the stage of ageing was conducted, the duration of ageing and temperature, at which the autoclave was present, are given in the Table. In individual experiments, the autoclave after filling by coal and gas was immediately was placed in a freezer; the curve of cooling was not recorded. In this case, the stage of cooling is not described in the table.

The $P-T$ diagrams experimentally obtained (Figs. 3, 4) allowed calculation of the pressure change that arises at the formation and decomposition of hydrates, and, consequently, the amount of methane absorbed or evolved at these processes. Having accepted the stoichiometric formula of the gas hydrate in the form of $CH_4 \cdot 6H_2O$, the amount of water in the gas hydrate can be calculated. For the comparison convenience, the registered amount of water in the hydrate (W_h) was calculated in percentages from the mass of dry coal and indicated in the last column of Table 2 for each experiment.

In the experiment with coal of the type K, the intense formation of hydrates was observed at the stage of cooling, herewith, the hydrate amount in the sample increased in the course of ageing at negative temperatures. Totally, about 40 % from the maximum content of water in the sample was turned into the hydrate. As the maximum water content in the sample, we mean the coal humidity that is achieved at its ageing in a desiccator with 100 % relative air humidity (above pure water). Earlier, experiments with coal of the type K selected from the outburst-prone XXVII seam of the Berezovskaya mine were conducted [23]. In this coal at the maximum humidity of about 3.1 up to 1.7 mass % of water participates in the formation of methane hydrate, up to 55 % of the maximum water content can turn into the hydrate. The coal of the same type K was selected from the neighbouring XXIV seam of the mine Pervomayskaya for the present work. The experiments with this coal considered in this work showed the results, similar to previ-
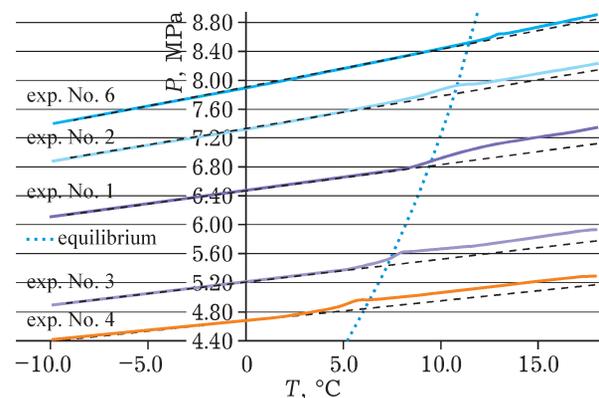

Fig. 4. Decomposition of methane hydrate. Curves of pressure change compared with the temperature inside the autoclave for the stages of increasing the temperature in exp. Nos. 6, 2, 1, 3 and 4, respectively (see Table 2). The equilibrium curve of methane hydrate is also shown.

ously obtained. In particular, the formation of gas hydrates in this sample occurs relatively fast, less than for an hour, overcooling in just several degrees is required for this. Note that in the course of the experiments performed earlier [23] we established that the process of hydrate formation was completed during 5−10 h, what and determined the selection of the ageing time of samples. The degree of overcooling, at which hydrates started to form, depended little on the absolute pressure.

In experiments with the coal of the type GZh, similar results were obtained, however, only of the order of 10 % from the maximum water content turned into a hydrate (see Tables 1 and 2). The results of experiments with coals 1G, 2G and D had a qualitative distinction from considered above. The hydrate formation at the stage of cooling at all investigated humidity values of samples of these coals was not registered in any of cases. For coal 1G with the maximum humidity, the hydrate formation at ageing for less 10 h was registered in trace amounts.

Prolonged experiments that showed that hydrate formation requires the time of the order of hundreds hours were set up, and even in this case the transformation degree of sorbed water into a hydrate does not exceed 15 % from its maximum content. We conducted experiments with coals 2G and D on humidities of about 75 % of maximal. The formation methane hydrate with coal of the type D was not registered even in case of prolonged ageing. A small amount of methane hydrates in case of coal 2G was formed even at ageing of 14 h. Thus, no less than 25 % from the maximum content of water in this coal can turn in methane hydrate. The experiment with the same sample on the formation in coal of CO_2 hydrate that demonstrated a somewhat larger transformation degree of water into the hydrate, in comparison with methane, was conducted.

$P-T$ curves presenting the dependence of methane pressure on temperature inside the autoclave for experiments, in which decomposition of methane hydrate when increasing the temperature was registered are shown in Fig. 4. According to the discussion given in the section "Experimental setup and method of measurements", the start of the step on the curve describing the pressure dependence from the temperature of the heat-carrier and end of the step describing the pressure dependence from the temperature in the centre of the autoclave corresponds to the experimental value of the temperature and pressure of the hydrate formation. The inflection shape and pressure step value are determined by the amount of released methane and value of free volume of the autoclave, as well as by the decomposition rate of gas hydrates, what determines the distinction in shapes of effects. The deviation of the start of ΔT_1 and ending of ΔT_2 of the phase transition from the equilibrium curve is shown in Table 3. Almost all the registered temperatures of the hydrates decomposition are somewhat higher than expected for the given pressure on the basis of the equilibrium curve of methane hydrate. It may be associated with sufficiently high heating rates that were used for the clear registration of steps on the curve pressure − temperature. Significant deviations of temperatures for coal 2G may be associated with a small amount of the hydrate formed in the given coal. Deviations that were observed for coals K and 1G are probably associated with imperfection of the experiment technique. These issues need further clarification.

CONCLUSION

It was shown in the work that water sorbed by various types of coals possessed a various ability to form methane hydrate. In coals of the type K that have the highest degree of metamorphization among the studied samples more than 50 % from the maximum water con-

TABLE 3

Deviation of the temperature of the start of decomposition (ΔT_1) and temperature of ending of decomposition (ΔT_2) of methane hydrate from the equilibrium curve

Nos.	Coal	W_s, %	W_h, %	ΔT_1, K	ΔT_2, K
1	K	2.26	0.70	0.3	2.4
2	GZh	4.35	0.50	0.5	0.1
3	1G	4.71	0.64	0.4	0.3
4	1G	4.71	0.52	0	−0.7
6	2G	7.56	0.20	1.6	1.4

tent is capable to formation of gas hydrate. In coals of the average degree metamorphism (coals G, GZh), a smaller fraction of water forms the hydrate, moreover, the process of the hydrate formation proceeds slowly. Coals of a low degree of metamorphism (D) are capable of sorbing a large amount of water, herewith; methane hydrates are not formed before to the humidity amounting to 75 % from limiting. As a whole, there is a trend to decreasing the proportion of water coupled into the hydrate and rate of the hydrate formation progressively as decreasing the degree of coal metamorphism. Thus, it was shown for the first time that coals with a different degree of metamorphism differ appreciably by the ability to form methane hydrate and require various approaches when conducting the experiment. Additionally, it was shown that water sorbed on coals was capable of forming CO_2 hydrate.

One may assume that the reason for this behaviour of coals is the increase of the number of functional groups on the surface of coal pores when decreasing the coal metamorphization degree. The number increase of functional groups leads to a stronger effect of these groups on sorbed water, herewith, almost the whole sorbed water turns out to be "tightly bound", *i. e.* hydrating directly functional groups of coal.

Acknowledgement

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Возможность формирования тонкоизмельченного угля при внезапных выбросах угля и газа, вызванных разложением газовых гидратов в угольных пластах

В. Г. СМИРНОВ[1], В. В. ДЫРДИН[1], А. Ю. МАНАКОВ[2], З. Р. ИСМАГИЛОВ[1,3], Т. П. АДАМОВА[2]

[1]Кузбасский государственный технический университет им. Т. Ф. Горбачева, Кемерово, Россия

E-mail: smirnovvg@mail.ru

[2]Институт неорганической химии им. А. В. Николаева Сибирского отделения РАН, Новосибирск, Россия

[3]Институт углехимии и химического материаловедения Федерального исследовательского центра угля и углехимии Сибирского отделения РАН, Кемерово, Россия

Аннотация

Разложение газовых гидратов метана в угольных пластах может быть одной из причин возникновения внезапных выбросов угля и газа. В работе экспериментально изучена возможность образования гидрата метана во внутреннем пространстве природного угля нескольких марок. Экспериментальные $P-T$ диаграммы для закрытой системы, содержащей влажный уголь и свободный метан, демонстрируют пиковое выделение метана в газовую фазу при пересечении кривой равновесия газовых гидратов. В образование газовых гидратов вовлекается менее половины сорбированной углем воды. Впервые показано, что с уменьшением степени метаморфизма угля снижается доля воды, способной вовлекаться в образование газовых гидратов, хотя общее количество воды, сорбируемой углем, увеличивается.

Ключевые слова: уголь, метан, гидраты, сорбция, десорбция, $P-T$ диаграмма, внезапные выбросы угля и газа