Full Length Article

# The formation of carbon dioxide hydrate from water sorbed by coals

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ABSTRACT

Experiments on the formation and dissociation of carbon dioxide gas hydrate formed from water that was adsorbed in two sub-bituminous coals and anthracite were carried out. Preliminarily, the coal samples were studied using various physicochemical methods. It was demonstrated that the conditions of the hydrate decomposition in coal do not differ substantially from the equilibrium conditions of carbon dioxide hydrate. In all the cases, the conversion of water to hydrate increases with increasing the pressure of the hydrate former and the initial humidity of coal samples. At the same time, it turned out that the amount of unreacted water in the sample also increases with an increase in the initial humidity of coal sample. A phenomenological model explaining the observed features of the hydrate formation in coal was proposed on the basis of the data obtained. In this model, the hydrate formation in coal is considered as a two-stage process: (1) a partial displacement of coal-sorbed water from the pore space into macropores and on the coal surface due to competitive sorption of carbon dioxide, and (2) the formation of hydrate from water droplets formed in the first stage.

## 1. Introduction

Coal, along with oil and natural gas, is one of the major sources of energy for modern civilization [1]. Coal is used to produce thermal energy, to generate electricity, and as a raw material for metallurgy. Methods of natural coal gasification and obtaining liquid hydrocarbons from coals are under development. Fossil coal is a solid hydrocarbon polymer with an extremely complicated chemical and elemental composition. The age of the majority of coal layers is 50–300 million years [2,3]. The organic mass of ancient plants was accumulated in marshlands in the form of peat, which was then covered with layers of sedimentary rocks. Coal was formed from buried peat during the metamorphism. The properties and features of coal are determined by characteristics of the plants from which the primary deposits were formed, by the duration of bedding, underground pressure of overlying rocks, layer temperature, the presence or absence of gas and water seepage through the layer, water acidity, as well as the chemical action of surrounding rocks and minerals. Carbon content in coal increases in the metamorphic sequence from bituminous coal to anthracite. Oxygen-containing functional groups are lost in the first stage of metamorphism and at the beginning of the medium stage [4], which is accompanied by

the evolution of a large amount of carbon dioxide. The medium and final stages of metamorphism involve an increase in the ratio of carbon to hydrogen (C/H) in the organic matter of coal, which is accompanied by the formation of methane [4].

Brown coals (lignites) are characterized by a high moisture-holding capacity. The equilibrium water content of lignites at 30 °C and a relative humidity of 96% reaches and often exceeds 25 wt% [5]. The moisture-holding capacity of bituminous coal and anthracite is within 5–15 and 1–5 wt%, respectively [2]. Brown coal is characterized by a high yield (30–35 wt%) of volatile substances released upon heating; the yield of volatiles from young bituminous coal is larger (40–45 wt%). In the sequence of coal metamorphism, the yield of volatile substances decreases to 20–25 wt% from coking coal and 8–10 wt% from anthracite [4,6]. The heat of coal combustion increases in the metamorphic sequence from 20 MJ/kg for brown coal to 35 MJ/kg for anthracite. The ash value of natural coal varies from one layer to another and does not correlate with the degree of coal metamorphism.

Natural coal has a developed and complicated pore system, which is formed in the course of coal metamorphism. The U-shape relationship between mesopore specific surface area (SSA) and volatile matter content (dry-ash-free basis, $V^{daf}$) is observed, demonstrating that the

number of mesopores within the lower rank coals ($V^{daf} > 15\%$) decreases with increasing coal rank and the coalification mainly affects the mesopore structure. For the higher rank coals with $V^{daf} < 15\%$, the mesopore size diminishes and the number of micropores ascends. Smaller mesopores and micropores gradually become dominant. This phenomenon is due to the effect of intensive compaction within bulk coal [7]. The average characteristic size of mesopores decreases in metamorphism sequence from 18 nm for brown coal to 3.5 nm for anthracite. The total pore volume increases with an increase in coal maturity degree [7]. The space of pores and cracks in undisturbed coal layer is occupied by water, methane, $CO_2$ and other gases that may be present in the sorbed and free states.

The concentrations and composition of gases in coal layers may vary within a broad range [8]. For instance, the average methane content of coal in the Donetsk basin is $14.7\,m^3/t$ of coal, while in some coal layers methane content exceeds 40 or even $100\,m^3/t$ of coal [9]. Methane content in the coal layers of the Kuznetsk basin is often $25–30\,m^3/t$ [10]. The most abundant components of coal-bed gas are methane and carbon dioxide. Coal layers occurring at a depth of less than 50–100 m are prone to weathering, so their gas phase contains mainly atmospheric nitrogen and carbon dioxide. With an increase in the depth of layer occurrence to several hundred meters, the fraction of methane in the gas of coal beds increases to 70% and more, while nitrogen content decreases substantially. In the Donetsk basin, in highly metamorphized coal layers, there is a rather extended zone in which the gas phase is represented only by carbon dioxide, its concentration reaching $35\,m^3/t$ of coal. Methane content in the coal layers occurring at a depth of 450–600 m in the Upper Silesian Coal Basin is 88–98%; nitrogen, $CO_2$, ethane, propane, argon, helium and other gases are also present [11]. As a rule, the sorption capacity of coal correlates with methane content in the coal bed. To ensure safety of coal mining from coal beds with a high gas content, preliminary degassing is required [12]. Degassing is hindered by a very low permeability of coal beds, especially in the undischarged state. The lack of information about the possible forms of methane occurrence in coal matter (except for sorbed and free methane) may be assumed in some cases [13]. Natural gas released during coal bed degassing (mainly methane) is used as a fuel; industrial methods for the production of coal-bed methane are being developed [10,12,14]. One of such methods is the displacement of coal-bed methane by carbon dioxide, which results in burying $CO_2$ as a harmful greenhouse gas [15,16].

Gas hydrates are inclusion compounds in which the molecules of gases or some readily volatile liquids occupy the cavities of the framework composed of hydrogen bonded water molecules [17]. One volume of a hydrate may contain up to 170 volumes of gas (STP). Hydrate-forming species may be represented by C1–C4 hydrocarbons, cyclopentane, carbon dioxide, inert gases, sulfur hexafluoride, tetrahydrofuran, etc. Gas hydrates widely occur in nature. Natural hydrates mainly contain hydrocarbon gases, carbon dioxide and nitrogen. According to the minimal estimations, the amount of gas in natural gas hydrates is comparable with the explored gas resources in the deposits of the conventional type [18]. At present, hydrates are considered as a promising source of hydrocarbons. Technologies for gas production from hydrate accumulations are under development [19]. The necessary conditions for the existence of the accumulations of hydrates are the presence of free hydrate-forming gases and water, a moderately high pressure and a decreased temperature. The information on thermobaric conditions necessary for the existence of gas hydrates is usually presented in the form of phase diagrams of the corresponding system: water – hydrate-forming agent (or a mixture of hydrate-forming agents). A large amount of data on the phase diagrams of hydrate-forming systems is reported in [17,20]. For example, the phase diagram of the water – carbon dioxide system is displayed in Fig. 1. In nature, thermobaric conditions necessary for the existence of hydrates occur in the upper parts of the sediments in water bodies at a depth of > 200–300 m and in the permafrost.
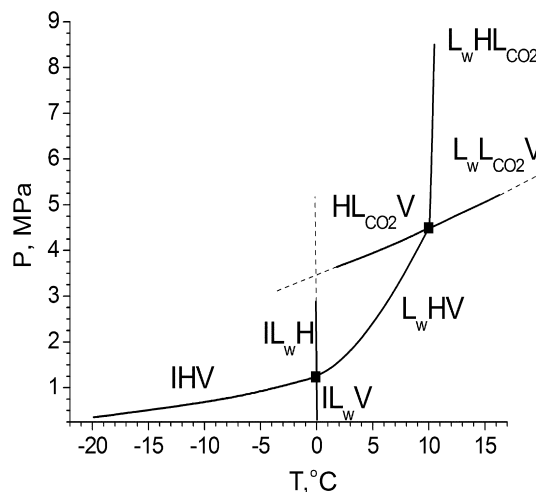


**Fig. 1.** T-P projection of the phase diagram of the carbon dioxide – water system. The data are taken from [17]. The phases are denoted as following: I – ice, $L_w$ – a saturated solution of carbon dioxide in water, H – hydrate, V – the gas phase, $L_{CO2}$ – liquid carbon dioxide. Squares are quadruple points.

Recently, a number of works appeared in which the possibility of the existence of gas hydrate inclusions in coal beds [21–23] or the possibility of the formation of such hydrates in the past [24,25] was discussed and substantiated experimentally. Evidently, free gas and water are present in coal beds. Thermobaric conditions favorable for the existence of hydrates may exist with the highest probability in coal deposits situated in the permafrost zone. These deposits exist at the north-east of Russia, in Alaska and in the northern part of Canada. As mentioned above, the gas in coal beds may contain not only methane but also large amounts of heavier hydrocarbons and carbon dioxide. The hydrates of these mixtures may be formed under softer conditions than methane hydrate, which broadens the region in which hydrates may exist. The presence of hydrates may affect the gas content of the coal bed, its permeability, sound velocity in the bed, etc., and thus they may alter the properties of coal bed substantially. A possible formation of carbon dioxide hydrates during $CO_2$-enhanced coal bed methane recovery is of definite interest, too [26]. For this process, carbon dioxide is pumped under high pressure into the coal bed to displace methane that is present in coal. At the coal bed temperature below 10 °C, carbon dioxide to be pumped into the coal bed may react with water present in coal to form the hydrate. Finally, some recent papers discuss the possibility to use hydrate formation in the coal matrix for gas storage and for the separation of gas mixtures [27–30].

The authors of [23,25] investigated methane hydrate formation in sub-bituminous to high-volatile bituminous coal at different moisture content. It was demonstrated that only a part of water present in coal may take part in hydrate formation; the formation of the hydrate itself occurs at a slight supercooling of the system, that is, the process is not hindered kinetically. It turned out that the equilibrium conditions for the hydrate in the coal matrix do not differ from those for the bulk hydrate. The authors of [25] studied the structure of the formed hydrate and did not find any differences from the structure of ordinary methane hydrate. In [27], the amount of gas sorbed on natural coal wetted with an aqueous solution of a surfactant was estimated. It was found that hydrate formation causes a substantial increase in the gas content of the system, and the presence of dissolved surfactant accelerates hydrate formation. Similar results for methane hydrate were obtained in [28]. Laboratory experiments on the separation of carbon dioxide and methane on a mixture of coal powder and water were carried out [29], as well as experiments on the separation of a gaseous mixture of methane, nitrogen and oxygen on the mixtures of coal powder with 1% solution of tetrahydrofuran [30]. It was stressed in both works that the process is complex in its nature, that is, the separation proceeds both due to gas