



Formation and decomposition of methane hydrate in coal



Vyacheslav G. Smirnov^{a,b}, Andrey Yu. Manakov^{c,d,*}, Elissa A. Ukraintseva^c, Galina V. Villevald^c,
 Tamara D. Karpova^c, Valeriy V. Dyrdin^a, Sergey Yu. Lyrshchikov^{e,f}, Zinfer R. Ismagilov^b,
 Irina S. Terekhova^c, Andrey G. Ogienko^c

^a Kuzbass State Technical University, Vesennaya Str., 28, Kemerovo 650026, Russian Federation

^b Institute of Coal Chemistry and Material Science SB RAS, Sovetsky Ave., 18, Kemerovo 650000, Russian Federation

^c Nikolaev Institute of Inorganic Chemistry SB RAS, Ac. Lavrentiev Ave., 3, Novosibirsk 630090, Russian Federation

^d Novosibirsk State University, Pirogova Str., 2, Novosibirsk 630090, Russian Federation

^e Kemerovo Science Center SB RAS, Sovetsky Avenue, 18, Kemerovo 650000, Russian Federation

^f National Research Tomsk Polytechnic University, Institute of Power Engineering, 30, Lenin Avenue, Tomsk 634050, Russian Federation

HIGHLIGHTS

- We studied formation of methane hydrate from adsorbed by coal water.
- Weakly bound part of adsorbed on coal non-freezing water can form methane hydrate.
- Coal surface does not change equilibrium conditions of gas hydrate formed on it.
- Hydrophilic areas of the coal surface may be active sites of gas hydrate nucleation.

ARTICLE INFO

Article history:

Received 16 May 2015

Received in revised form 19 October 2015

Accepted 29 October 2015

Available online 3 November 2015

Keywords:

Gas hydrate

Methane

Coal

Water adsorption

ABSTRACT

The formation of methane hydrate from water adsorbed on the surface of natural bituminous coal has been studied. The state of the adsorbed water has been examined with DSC and NMR techniques. The isotherm of adsorption of water on coal has been studied. The experiments have shown that the water adsorbed on the coal studied is bound and non-freezing, i.e., no ice formation and melting occurs on cooling and heating of the coal samples containing the adsorbed water. This water undergoes a glass-like transition. The adsorbed water can be divided into strongly bound and weakly bound, in accordance to known models of water sorption by coals. Cooling and heating of containing adsorbed water coal samples under methane pressure results in expressed pressure anomalies corresponding to the formation and decomposition of the methane hydrate. Thus, the non-freezing water is capable of forming gas hydrate. It has been demonstrated that the hydrate is formed only from the weakly bound water. The equilibrium pressure and temperature parameters of this hydrate are identical to those of the bulk hydrate. Thus, it has been shown that at proper pressure and temperature gas hydrates can be formed in coals even in absence of free water. The results obtained make possible to suggest that the hydrophilic areas of the coal surface are active sites of gas hydrate nucleation.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Gas hydrates are clathrate compounds featuring molecules of hydrate-forming gas included in the cavities of polyhedral framework built from water molecules. One part of methane hydrate

can contain up to 170 parts of gas V/V [1]. Gas hydrates can be formed by lowest hydrocarbon homologues (C1–C4), carbon dioxide, nitrogen, oxygen, etc. Under moderate pressures the majority of gas hydrates can exist only at temperatures below 20 °C. Commonly, pressure increase results in higher hydrate decomposition temperatures. For example, equilibrium pressures over the pure methane hydrate are 2.51 and 6.95 MPa at 0 and 10 °C, respectively. For heavier gases the pressure is lower. So, equilibrium pressure of carbon dioxide at 0 °C is 1.24 MPa and 4.49 MPa at 10 °C. Hydrates formed by gas mixtures are often characterized by low equilibrium pressures. At 10 °C the equilib-

* Corresponding author at: Nikolaev Institute of Inorganic Chemistry SB RAS, Ac. Lavrentiev Ave. 3, Novosibirsk 630090, Russian Federation. Tel.: +7 (383) 316 53 46; fax: +7 (383) 330 94 89.

E-mail addresses: smirnovvg@mail.ru (V.G. Smirnov), manakov@niic.nsc.ru (A.Yu. Manakov).

rium pressures for methane containing 1% and 2.6% of propane are 4.36 and 3.01 MPa, respectively (data of Ref. [1]).

Hydrates of hydrocarbon gases (basically, of methane) are abundant in nature making them a promising source of fuel gas [2]. Currently, the technologies of natural gas extraction have been successfully tested at permafrost gas hydrate deposits, as well as sea deposits of gas hydrates [3,4]. The prerequisites for formation and existence of natural gas hydrates are proper pressure (P) and temperature (T), combined with presence of free gas (or sufficiently concentrated aqueous solution). These conditions are found in sea or ocean sediments or sedimentary strata cooled with permafrost. The relevant depth range is termed gas hydrate stability zone (GHSZ) [5]. The minimal basin depth sufficient for existence of the hydrate at the bottom is ~ 200 m for north seas and 500–700 m for equatorial areas. The thickness of GHSZ can reach one kilometer. In permafrost the thickness of GHSZ is 400–800 m (sometimes over 1 km), the lowest occurrence depth is about 250 m. In permafrost, so-called relic hydrate conglomerations, existing due to self-preservation of metastable hydrates in frozen rock, can be found above GHSZ [6].

Coal is one of the most common fossil fuels. It has been formed by complex transformations of organic matter during millions of years. The process of coalification was an unremitting geochemical evolution, starting with decay of organic materials in swamps and followed by their metamorphosis under influence of geological forces (lithostatic pressure, temperature and tectonic shear forces). When water-logged peat bed is covered by impervious layer of sediment, the situation strongly resembles the conditions in an autoclave: the peat material is slowly transformed by chemical reactions. In essence, the coalification can be considered as essentially a dehydration process probably followed by successive decarboxylation and demethanation [7]. These processes afforded carbon material possessing a complex multi-level structure [7]. At the bottom, it comprises macromolecules having polyaromatic core. It is decorated with various functional groups (carboxyl, carbonyl, etc.). With increasing coal rank the content of the aromatic carbon grows and functional groups are extinguishing. These macromolecules are joined in agglomerates of complex architecture. The space between the agglomerates is organized in a complicated system of pores with dimensions ranging from micro to macro. Some models postulate that the peripheral functional groups of the macromolecules are mostly located at the surface of the coal pores [8]. Overall porosity of coal is 25–30% in subbituminous coals, 1–3% in bituminous coals containing 87–89% of carbon, and about 10% in anthracites. In general, the surface of the coal includes strongly hydrophobic, weakly hydrophobic, and hydrophilic areas.

Because of the porous nature and diverse chemical decoration of the surface coal is an excellent sorbent. Gas and water present in coals are almost entirely in the adsorbed state. The term coal bed methane designates the gas from coal strata commonly containing 90–97% of methane with admixtures of light hydrocarbons (C1–C4), carbon dioxide, hydrogen sulfide, and nitrogen. Sometimes the fraction of heavy hydrocarbons can be essentially higher [9]. During the early stages of the coalification process, coal bed methane is slowly generated until a threshold is reached in the bituminous ranks. Additional methane generation serves as the driving force to expel excess gas into the macropore network. It is generally accepted to consider three types of coal-bed methane: free (in macropores), adsorbed, and dissolved in pore water [10]. Currently, the existence of methane solid solution in crystalline coal substance has been acknowledged [11].

Three main types of water–coal bonds occur: water adsorbed by physicochemical forces, free water held by mechanical forces, and chemically bound water. Water adsorbed by physicochemical forces is strongly bound to oxygen surface functions (hydroxyl,

carboxyl). The model considered in the studies [12,13] suggests that the primary sorption of water in coals occurs exactly at these oxygen-containing groups. From the chemical viewpoint, this water is involved in the first hydration sphere of polar groups and is strongly bound. Secondary hydration corresponds to development of water cluster at these primarily hydrated polar groups. The micropores are filled with water at the last stage of the sorption. Depending on the structure and composition of a given coal sample, the properties of water held by secondary sorption and in micropores can differ in a certain extent from those of bulk water. For example, in the high-rank coals all adsorbed water undergoes a glass-like transition instead of common freezing [14]. It is well-known that the sorption of water and methane are competitive; the presence of water in coals decreases the sorption capacity of CO₂ or CH₄ gases [15,16].

The hypothesis on possible existence of gas hydrates in coal beds was formulated some 40 years ago by discoverer of natural gas hydrates Makogon [17]. Later this possibility has been sporadically discussed in the literature, the authors of this contribution being involved too [18,19]. The formation of a hydrate in the coal bed requires the pressure and temperature matching the stability field of the hydrate formed by the coal bed gas. It is noteworthy that sometimes the coal bed gas is enriched with carbon dioxide, ethane and propane [9]. The hydrates of these gases and their mixtures can exist under milder P – T conditions as compared to pure methane. One can expect that the hydrates of coal bed gases may occur in permafrost coal beds, such as Pechora coal-basin (Russia) or north-canadian coal deposits. The analysis of thermobaric conditions in coal beds is beyond the scope of this study, however, reference literature gives several examples of thermobaric conditions corresponding to the stability region of the methane hydrate. Among the strata of the Kuznetsk coal basin they include the Severnaya coalmine, Vladimirovskii bed ($P = 4.8$ MPa, $T = 278$ K), Sarabalinskaya coalmine, bed 11 ($P = 5.1$ MPa, $T = 279$ K) (personal communication). The decomposition temperatures of the methane hydrate at $P = 4.8$ and 5.1 MPa are 279 and 279.8 K, respectively [1]. In the Pechora coal basin about 80% of coal beds have pressures and temperatures matching the stability of the methane hydrate (personal communication). Therefore, the idea about possible existence of gas hydrates in some coal beds looks quite sound. Besides, currently carbon dioxide disposal combined with coal bed methane extraction is under discussion [20]. The injection of carbon dioxide in a bed is likely to result in pressures higher than the original bed pressure. Keeping in mind that the carbon dioxide hydrate is formed at lower pressures than the methane hydrate, as well as possible cooling of the bed on injection, the development of technogenic carbon dioxide hydrate in these beds is rather probable.

The development of gas hydrate storage of natural gas, as well as separation of gas mixtures, currently is considered as highly topical [21,22]. One of the suggested approaches to acceleration of hydrate formation reaction is its realization in water dispersed in a suitable matrix, thus providing high area of the water–gas interface. Charcoals were proposed as the matrix for storage of gases in the hydrate form [23–25]. The authors succeeded in high conversion of the water in the charcoal pores in the hydrate. The equilibrium conditions of this hydrate were the same as for the bulk sample. In recent years the fossil coal and nanoporous carbon materials are studied as the medium for storage of methane and carbon dioxide [26–28].

All the above indicates that examination of hydrate formation in coals is highly topical. On the other hand, the literature is scarce on physical–chemical studies on hydrate formation in the matrix of natural coal; the available literature is cited above. As noticed above, water and gas can occur in natural coals in many forms. Gas hydrates can be considered as yet another form of occurrence

Download English Version:

<https://daneshyari.com/en/article/6634197>

Download Persian Version:

<https://daneshyari.com/article/6634197>

[Daneshyari.com](https://daneshyari.com)