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Evidence for and thermodynamics of coal mine methane formation in catastrophic events by the hydrolytic disproportionation of carbon

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This paper evaluates the thermodynamic possibility of coalbed methane formation as a result of direct reaction of coal and water during the process of hydrolytic disproportionation of carbon (HDC). Some examples of experimental and natural evidences of HDC are discussed.

Introduction

Coal mine methane (CMM) is a general term for all methane released mainly during and after mining operations (Karacan et al., 2011). The mechanism of methane formation is a key for a understanding the reasons for accumulation of its “huge reserves” and its role in “unpredictable catastrophes” (Ettinger, 1988). The main issue is a lack of clear-cut evidence for the source of hydrogen for rapid methane formation and its large scale accumulation. Traditionally, three mechanisms for methane formation are proposed: (1) non-biogenic, (2) by the activity of anaerobic bacteria during plant material deposition and early stages of diagenesis, and (3) from pyrolysis of coal material during coal maturation (Hucka and Bodily, 1993). All three mechanisms do not adequately explain the rapid and unpredictable accumulation of huge amounts of the gas in the processes of exploration of coal deposits. The processes that lead to catastrophic events are also not quite clear until now. In the reaction that produces coalbed methane, the two final products are methane and carbon dioxide and one of the reactants is coalbed carbon. Coal contains some amounts of hydrogen and hydrocarbons but these quantities are not enough for the balance of an equation. The main question is the source of the huge amounts of hydrogen and oxygen and the most reasonable answer is water. Therefore this process could be explained by direct formation from coal and water (Vigdergauz, 2011).

A proposed mechanism of rapid methane formation and evolution of huge amounts of the gas during exploitation of coal deposits is hydrolytic disproportionation of carbon (HDC) similar to the processes which are observed under the hydrolytic disproportionation of organic matter (HDOM) in formation of kerogens. Most of the HDOM examples presented in this paper are adopted from Helgeson and his group (Helgeson et al., 2009; Helgeson et al., 1993) which proposes that (i) the concept of a thermodynamically metastable equilibrium as the foundation of hydrolytic disproportionation (ii) the water and oil are chemically linked, and maintain a metastable equilibrium among themselves via oxidized carbon species (such as CO_2)

exchanging hydrogen and/or oxygen with one another, as determined by the oxygen and/or hydrogen fugacity of the system and (iii) the process wherein this metastable equilibrium was achieved and maintained was defined as a reaction of a hydrocarbon (HC) of a given oxidation state with water to produce organic species having higher and lower oxidation states.

Water and organic matter, including hydrocarbons, in HDOM, easily exchange hydrogen or oxygen with one another under certain conditions. The process appears to take place via well-known organic chemical redox-reaction pathways and is most evident in open-fluid systems. HDOM is suggested as an unrecognized geologic agent of fundamental importance (Price and DeWitt, 2001). Although the overall process is irreversible, HDOM was theorized to involve both reversible and irreversible intermediate reactions, depending on system conditions. The end products of this overall process are CO_2 and CH_4 .

The aim of this paper is to evaluate thermodynamic possibility of methane formation directly from coal and water during the exploitation of coal deposits.

Short history of the catastrophic events

Catastrophic events due to methane explosions during coal mining are well documented but ill-understood. The explosions at Senghenydd, South Wales coalfield, UK (14 October 1913), Courrieres Mine, Northern France (10 March 1906) and Benxihu Colliery China (April 26, 1942), killed 436, 1,099 and 1,549 miners (including many children) respectively (Dhillon, 2010). The World's worst mining accidents of the past decade occurred in Zasyadko coalmine, Donetsk, Ukraine (19 November 2007, 80 fatalities), Ulyanovskaya coalmine, Kemerovo, Russia (19 March 2007 - 108 fatalities), and Haizhou shaft, Fuxin, China (14 February 2005, 214 fatalities). Deaths were mainly caused by carbon monoxide poisoning and asphyxiation. CMM, entering a mine can create a localized zone of high concentration in an area of low air velocities and cause a serious threat to mining safety and productivity (Karacan, 2011). Methane concentration is monitored by providing adequate ventilation in underground coal mines so that its levels are kept well below the explosive limit of 5% to 15% (in this range, methane can be ignited easily in the presence of an ignition source to create a violent methane explosion that may propagate in the presence of combustible coal dust).

During catastrophic events there is sudden observed emission of methane and carbon dioxide. The volume of the emitted gases in some cases could reach hundreds cubic meters per tonne of the thrown

coal. One of the biggest sudden emissions of gases from coal occurred in 1921 in France in the Gard district at the mine Nord' Alle (Ettinger, 1988). The sudden outburst of a large amount of carbon dioxide flooded the mine, poured on the surface and submerge small town situated in the lowlands.

Coal composition

The types of coal, classified generally based on the content of volatiles and carbon concentration are anthracite, bituminous coal, subbituminous coal, and lignite (Kopp, 2012). However, the exact classification varies between countries. The lowest rank coal lignite (or brown coal) is almost exclusively used as fuel for electric power generation. According to the German classification lignite contains an average of 60 -75% carbon, 6.0-5.8% hydrogen and 34-17% oxygen. Bituminous coal is dense, black - dark brown often with well-defined bands, used primarily as fuel in steam-electric power generation and to make coke. Anthracite, the highest rank of coal is a harder, glossy, black coal used primarily for residential and commercial space heating. It may be divided further into metamorphically altered bituminous coal and petrified oil. Anthracite contains more than 91.5% of carbon, less than 3.75% of hydrogen, and less than 2.5% of oxygen.

Evaluation of the influence of coal rank and pressure on the sorptive capacities shows that under pressure and as coal matures the sorptive capacity increases. For example at the pressure 42 atm the adsorbed methane content in anthracite is near 28.3 scm/ton (dry, ash-free) and in medium-volatile bituminous coal is near 17 scm/ton (dry, ash-free) (modified from Al-Jubori et al., 2009). At the same time methane generation by microbial activity (biogenesis) is maximal for sub-bituminous coal and thermally derived methane is characteristic of bituminous coal (Al-Jubori et al., 2009).

Electrochemical differences of the redox-states of coals which are influenced by the balance of hydrogen and oxygen within them are shown in Figure 1 (N.K.Gromova and V.E.Vigdergauz, Unpublished Results, May 1982).

HDOM is a redox- reaction that could be electronically balanced by assigning nominal oxidation states to carbon as a function of various carbon bonds (Helgeson et al., 1993). Methane is the most reduced hydrocarbon (HC) possible, with a value of -4. In the model of HDOM, oxidation-reduction reactions must be balanced. If some carbon species are being oxidized, then other carbon species must be reduced, and they are reduced to methane and other lower-molecular-weight hydrocarbons.

Kerogen, a mixture of organic chemical compounds that make up a portion of the organic matter in sedimentary rocks, is insoluble in normal organic solvents because of the large molecular weight of its component compounds. The soluble portion is known as bitumen. When heated to the right temperatures in the Earth's crust, (oil window ca. 60–160 °C, gas window ca. 150–200 °C, both depending on how quickly the source rock is heated) some types of kerogen release HCs.

Like coal, kerogen is a mixture of organic material, rather than a specific chemical. It cannot be given a chemical formula and its chemical composition can vary distinctively from sample to sample. For example kerogen from the Green River Formation oil shale deposit of western North America contains elements in the proportions carbon 215 : hydrogen 330 : oxygen 12 : nitrogen 5 : sulfur 1 (Chilingar, 1976). Kerogens with high (H/C)s are consistent with the widely

Figure 1. Maturation of coal influences on the dependence of its electrochemical potential (mV with respect to the silver – silver chloride reference electrode) from the pH value.

recognized empirical association in source rocks of high petroleum generation potential with high H/C of the immature kerogen from which it forms (Tissot and Welte, 1984; North, 1985; Hunt, 1995). Any water originally present (or subsequently entering) the source rock will react irreversibly with the mature kerogen to produce petroleum and CO₂ gas in accord with the hydrolytic disproportionation reaction represented by (Helgeson et al., 2009):

where the subscripts (s), (l), and (g) represent the solid, liquid, and gas states, respectively.

Reaction (1) will proceed irreversibly until essentially all of the water originally present in, or subsequently entering, the source rock is consumed. Although this reaction generates petroleum, it should be emphasized here that prior to the onset of oil generation in a hydrocarbon source rock, any water initially present in or subsequently entering the system may react with the kerogen in the source rock to produce CO₂ gas and a new kerogen with a higher H/C than that of the reactant kerogen, depending on the compositions of the reactant and product kerogens and the temperature, pressure, and the fugacities of CO₂(g) and H₂(g) in the source rock.

The following observations were made by Helgeson et al. (2009)

1. If water encounters this kerogen at 150°C and 820 atm, it will react irreversibly with it to produce petroleum and/or CO₂ gas until either all of the water or the kerogen is consumed by the reaction. The mature kerogen may react with water to produce CO₂ gas and another kerogen with a higher H/C.
2. With increasing mining depth, temperature and pressure are also increased and for the depth 5-6 km temperature reaches 200°C and pressure for an average density 2.26 g/cm³ becomes near 1200-1400atm. For such conditions among n-alkanes methane becomes a favorable phase.
3. Irreversible generation of methane illustrate the fact that the isopleths for the n-alkanes with carbon numbers <4 extend beyond the unit activity limit at fugacities of oxygen which are lower than those compatible with crude oils can be attributed to their inability to achieve metastable equilibrium with the higher molecular weight hydrocarbon species in petroleum at the pressures, temperatures, and fugacities of hydrogen obtaining in hydrocarbon source rocks. This can be demonstrated by first writing, for example, the overall hydrogenation reaction represented by:

and

In all such cases, the required hydrogen cannot be generated in the absence of H₂O by the maturation of crude oil because the anhydrous maturation process itself consumes H₂(g) as higher-molecular weight hydrocarbons react to form lower-molecular weight species. In contrast, if crude oil is in pervasive contact with water (as it probably is during and after migration to the reservoir), methane can be generated irreversibly by hydrolytic disproportionation of liquid hydrocarbon species in crude oil (Helgeson et al., 1993) and/or kerogen (Seewald et al., 1998; Snowdon, 2001). This can be demonstrated by first writing the hydrolytic disproportionation of (for example) n-decane as which produces 31 mol of H₂(g) for each mole of liquid decane consumed. Using an analogous procedure for the n-eicosane species in crude oil (C₂₀H₄₂(l)) and the mature kerogen represented by C₁₂₈H₆₈O_{7(c)} leads to the reactions (Helgeson et al., 2009):

and

Although these reactions and others like them are limited in the presence of water only by the supply of the reactant kerogen and/or hydrocarbons in crude oil, the fact that they produce from 23 to 45 mol % CO₂(g) is inconsistent with the composition of natural gas, which generally contains <10 mol % CO₂(g) (Lundegard and Land, 1989; Smith and Ehrenberg, 1989; Poulson et al., 1995; Selley, 1997). Seewald et al. (1998) reached the same conclusion by comparing their experimental results with the composition of natural gas.

However, they suggest that the present CO₂ content of thermogenic natural gas is a vestige of secondary processes such as reactions with minerals that remove CO₂ from the gas and precipitate

calcite. Their material balance considerations support this possibility. Using experimentally derived kinetic parameters, Seewald et al. (1998) also concluded that the bulk of methane, ethane, propane, and butane production in natural gas occur deep within sedimentary basins at temperatures in excess of 160°C.

It appears that generation of dry gas (methane) is kinetically favored at high temperatures (Snowdon, 2001), which is consistent with the fact that methane predominates by far in deep-basin natural gas (Price, 1995, 2001). Although highly variable, the methane content of natural gas ranges up to 95 mol % or more (Hamak and Sigler, 1991; Mango et al., 1994; Price, 1995; Mango, 1996; Selley, 1998; Snowdon, 2001).

The calculations of Helgeson et al. (2009) summarized above indicate that oil generation may occur at high and/or low temperatures depending on the presence or absence of water and the bulk composition of the reactant kerogen, which contravenes the concept of a limited "oil window".

Therefore the main differences in the compositions of coals and kerogens are the proportions of hydrogen and oxygen in them. Kerogens, in comparison with coals, contain much more hydrogen and for the methane formation from coal the role of water as a source of hydrogen increases.

Thermodynamics of HDC

A Gibbs free energy change under standard conditions is equal to total energy change for system minus energy lost in its disordering:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (6)$$

There are two common methods of calculating ΔG° of chemical reactions - determine ΔH°_{rxn} and ΔS°_{rxn} and use Gibbs equation or use tabulated values of free energies of formation, ΔG°_f . Table 1 summarizes molar thermodynamic characteristics of substances (Robie et al., 1979; Chao and Zwolinski, 1978) that were used for the calculations.

Table 1. Standard molar thermodynamic characteristics of substances.

Substances	$\Delta H^\circ_{f, 298}$ kJ/mol	ΔS°_{298} J/mol·K	$\Delta G^\circ_{f, 298}$ kJ/mol
C (s)	0	5.74	0
H ₂ O(l)	-285.830	69.95	-237.141
O ₂ (g)	0	205.15	0
CH ₄ (g)	-74.81	186.26	-50.708
CO(g)	-110.53	197.67	-137.171
CO ₂ (g)	-393.510	213.79	-394.375
CH ₃ COOH(g)	-432.25	283.36	-374.33
(CH ₃ COOH) ₂ (g)	-927.68	414.28	-766.38

HDC or direct reduction of hydrogen from its oxide by coal in the form of carbon could be represented by the equation:

The above reaction 7 is an endothermic one, but the products entropy increases and the reaction could be product-favored. Changes of the reaction 7 entropy $\Delta S^\circ_{rxn} = 248.67 \text{ J/mol·K}$ is positive and this reaction could be "entropy driven". From the practice of coal mining it is frequently observed that the temperature of a coal bed decreases

before a sudden emission event (Ettinger, 1988) suggesting that the cooling was due to the endothermic character of the processes.

One of the main pathways for methanogenesis is acetate fermentation (Fukuzaki et al., 1990; Powell et al., 1983). Acetate is the major intermediate in the bioconversion of organic matter to CH_4 and CO_2 and about 70% of the total methane produced in anaerobic digestion originates from acetate (Gujer and Zehnder, 1983). Studies of the kinetics of the methanogenic fermentation of acetate show that the undissociated form of acetic acid functions not only as the real substrate but also as the unavoidable inhibitor, depending on its concentration, for aceticlastic methanogens (Fukuzaki et al., 1990). Bioprocesses are too slow in comparison with the rapid process of HDC methane formation during catastrophic events for which bacteria are not required.

Reaction 7 could proceed through the endothermic stages of acetic acid and its dimers and polymers intermediate formation:

Dimers of *trans*-configuration of acetic acid are preferable and more stable forms of the acid and at room temperature and atmospheric pressure its vapor contains 97% of dimers (Chao and Zwolinski, 1978). Molecular structure of the dimer of acetic acid contents circle from eight atoms, but taking into account the short length of the hydrogen bonds and small dimensions of hydroxyl groups, this circle in size becomes very similar to the circles of carbon atoms of the carbon benzenoid structure with three-, four-, and five-fused benzene rings, and other structures with a single benzene ring.

The size and tetrahedral structure of methane molecules, similar to the stereochemistry of water clathrates, gives additional features of favorable stereochemistry during the formation of intermediate stereo-structures of hydrotated coal rings, acetic acid like dimers and polymers and their subsequent transformation and decomposition with the production of methane and carbon dioxide as final substances. Stereo chemical processes favour the shift of reaction 7 to products leading to the situation when small methane and carbon dioxide molecules are trapped inside “cages” of hydrogen bonded water molecules with possible formation of clathrate hydrates.

Necessary energy for the reaction 7 could be produced by exothermic combustion processes of partial oxidation of methane, such as:

Summary processes of the generation of methane in a coal bed and its explosive oxidation are highly exothermic. A simplified scheme (Fig.2) (Vigdergauz, 2011) could illustrate an energy change during the process of formation and subsequent explosion of coal methane.

The sum energetic effect of carbon oxidation through the process of methane formation is near 400 kJ/mol of carbon. Reaction energy is undependable from its path and direct oxidation of carbon by oxygen on the combustion reaction:

has the same energy. The differences are in the reaction path only and in the values of the activation energies for stages.

Fig. 2

HDC as a process of coal gasification can include different sub-reactions and stages which depend on the initial temperature and pressure in the coal bed and its composition that includes moisture, volatile matter and catalyst content. Some of these stages, such as gasification reaction:

are endothermic with an enthalpy ΔH of about 120-160 kJ/mol, others, such as the “shift conversion” reaction:

and the reaction of hydrogasification:

are moderately exothermic with an enthalpy of about 32-88 kJ/mol, and, finely, a strong exothermic stage - combustion reaction 11 with an enthalpy 393,51 kJ mol⁻¹.

Critical conditions of the HDC

By Gibbs equation 6 it is possible to evaluate a critical temperature of methane formation from coal by its direct interaction with water in reaction 7. Free energy of the reaction 7 becomes equal to zero under the temperature 415.57 K or ~ 142°C. This temperature might be considered as a critical for methane and carbon dioxide irreversible formation under the normal pressure.

Usually temperatures near 140°C are characteristic for the depths near 4 km (Helgeson et al., 2009), but various mining and geological peculiarities could drastically change the situation. Influence of the drop pressure during exploitation of coal deposits could be illustrated by the mentioned earlier common knowledge (Ettinger, 1988) that “if you do not touch the coal bed no methane escape will be observed”.

The most successful industrial exploitation of coalbed methane occurs primarily in coals of the Fruitland Formation (Gas Technology Institute -GTI, 2002; Pashin and McIntyre, 2003). About 2,550 wells were operating in the San Juan Basin in 2001. All wells are vertical wells that range from about 500 to 4,000 feet in depth, and were drilled using water or water-based muds. Almost every well has been fracture-stimulated, using either conventional hydraulic fracturing in perforated casing or cavitation cycling in open holes. Each fracture stimulation treatment may inject, on average, approximately 55,000 to 300,000 gallons of stimulation and fracturing fluid per treatment. Total gas production was 925 Bcf in 2000 (GTI, 2002).

Reactivity of water

An understanding of the reactivity of organic molecules of coal

in hot water could be developing similarly to that of kerogen (Price and DeWitt, 2001) from studies aimed at explaining how organic matter forms in natural environments and then breaks down. In natural systems where coals are depolymerized, hot water is ubiquitous and usually contains salt and minerals. Reactions such as ionic condensation, cleavage, and hydrolysis are facilitated by changes in the chemical and physical properties of water as temperature increases. These changes make the solvent properties of water at high temperature similar to those of polar organic solvents at room temperature, thus facilitating reactions with organic compounds.

By conventional thought, most organic compounds do not react with water. If, however, temperatures are raised to 250–350°C, reactions do proceed (Siskin and Katritzky, 1991). At such temperatures, water density decreases from 0.997 to 0.7813 g/cm³, the dielectric constant falls from 78.85 to 19.66, the solubility parameter decreases from 23.4 to 14.5 (cal/cm³)^{1/2}, and the dissociation constant increases from 10^{-13.99} to 10^{-11.30}. These changes in physical properties make the solvent properties of water at 300°C roughly equivalent to acetone at 25°C, thus increasing the favorability of ionic reactions of organics in water (Siskin and Katritzky, 1991). Also, an increase in the dissociation constant of water will increase the rate of acid- and base-catalyzed reactions in water far above the effect of increased temperature alone. Ionic chemistry predominates as high-temperature water opens reaction pathways that are alternate to, and preferred over, thermal (free-radical) routes. In conditions of high pressure and temperature which are characteristic for methane explosion the reduction of hydrogen from water might be described as a chain-type reaction on the free radical-mechanism (Vigdergauz, 2011):

According to Price and DeWitt (2001) HCs ionic-based reactions easily proceed between water at high-temperature, and saline water that leads to hypothesis that HDOM takes place via ionic-based reactions. Formation of carbonium ions may further aid breakdown of organic compounds (Roberts and Caserio, 1964). The carbonium ion, a positively charged carbon cation, is unstable and quickly reacts with a negatively charged species. Carbonium ions thus provide a pathway for covalently bonded organic compounds to react with ionic species.

Helgeson et al. (2009) demonstrated that (i) oil generation takes place in window between ~50 and ~160°C (Tissot and Welte, 1984; Hunt, 1996), and a further increase in temperature leads to thermal destruction of oil and generation of natural gas; (ii) the irreversible reactions that drive the metamorphic process will lead, in accordance with the second law of thermodynamics, to a state of metastable equilibrium that will coincide with a metastable minimum Gibbs free energy for the system.

Kinetics and catalytic phenomena

The results of thermodynamic calculations and Gibbs free energy minimization computer experiments carried out to characterize this minimum do not coincide with geologic reality (Price and DeWitt, 2001). Therefore we must conclude that, in accord with the

conventional paradigm, the process of oil generation is indeed kinetically controlled in a state that is far from equilibrium. Otherwise, it can be regarded as an irreversible process that leads to successive states of metastable equilibrium within the time frame of basin subsidence.

By the detailed analysis of the kinetics of methane and tar evolution during coal pyrolysis (Holstein et al, 2005) for coals coming from different geographic locations (South Africa, South America, Europe, Australia, and North America) it has been shown that the temperatures at which the evolution of methane and tar begins (T_{ini}), and the temperatures at which the evolution rates reach a maximum (T_{max}), reveals a correlation between the T_{ini} for methane and T_{max} for tar. This may be due to the fact that both tar and methane evolve as a result of similar reactions involved in the breakup and recombination of the coal macromolecular network. The study was done by employing a thermo-gravimetric analyzer coupled with a Fourier-transform infrared spectrometer (TG-FTIR). This TG-FTIR data for tar evolution reveal a generally consistent behavior for coals from different parts of the world, showing increasing activation energies with increasing coal rank.

In the case of petroleum generation and maturation in sedimentary basins (Helgeson et al. 2009) catalysts include mineral surfaces (e.g., Jurg and Eisma, 1964; Shimoyama and Johns, 1972), rock chips (Lewan, 1993), H₂O (Siskin and Katritzky, 1991; Lewan, 1993, 1997), and transition metals (Mango, 1992, 1996, 2001; Mango et al., 1994; Mango and Hightower, 1997). Partially similar to the HDC process, is a Fischer–Tropsch process for which a variety of catalysts can be used, but the most common are the transition metals cobalt, iron, and ruthenium (Balonek et al., 2010). Nickel can also be used and this catalyst tends to favor methane formation (“methanation”). A High-Temperature Fischer–Tropsch (or HTFT) process is operated at temperatures of 330°C–350°C and uses an iron-based catalyst. Low-Temperature Fischer–Tropsch (LTFT) is operated at lower temperatures and uses a cobalt based catalyst. It is reasonable to conclude that mineral impurities of coals mentioned above will also be catalysts of the HDC processes.

Natural and experimental evidence for HDC

By application of thermodynamic simulation, Pavlov et al (2006) analyzed carbon disproportionation and fractionation in the carbon-water-gas system close to atmospheric conditions at a temperature of 25°C and a pressure of 1 atm. It was shown that the aqueous solution and the gas phase become enriched in carbonate and in methane, respectively.

The proposed path of methane formation on the reaction of water with coal is confirmed by the results of environment chemical analysis. By an extensive study of the hydrologic situation in the Fruitland Formation, it was shown that the continuity of water coverage of the formation is a crucial question for the formation of methane from coal-beds (Fehn et al., 2001). Shvartsev et al. (2006) have recently shown for the Erunkovo region of the Kuznetsk Basin (Russia) that during the coal methane formation a high mineralization of water and the higher contents of HCO₃⁻ is mainly observed due to CO₂ formation, which is not the product of mantle genesis but is the product of coal metamorphism. The Khibina and Lovozero alkaline massifs of the Kola Peninsula, and rocks from alkaline massifs in Siberia

contain considerable amounts of HC gases, especially in their fluid inclusions (Ikorskii and Romanikhin, 1964).

Most examples in this paper were condensed from (Price and DeWitt, 2001). The hypothesis of hydrolytic disproportionation of coal could be supported by experiments carried out in gold bags containing water, ethane, ethene, and the naturally occurring mineral buffer pyrite–pyrrhotite–magnetite, which set the oxygen(hydrogen) fugacity of the system (Seewald, 1994). When experimental conditions were modified by injecting ethane, ethene, or water into the system, or by changing temperature, the ethane/ethene ratio in the system gradually changed towards the equilibrium ratio expected from thermodynamic calculations. The concentrations of CH_4 , CO_2 , H_2S , and H_2 also changed accordingly, demonstrating that carbon-carbon bonds were being broken. Ethane, ethene, water, the mineral buffer, and other dissolved species were all in metastable equilibrium, which was maintained by the species exchanging hydrogen and/or oxygen with one another (Seewald, 1994). Also, HCs were produced from water and acetic acid, while experimentally examining aqueous acetic acid thermal stability (Palmer and Drummond, 1986; Bell et al., 1994). Hoering (1984) deuterated both shale kerogen and HCs (*n*-docosane, *n*-C22; and 1-octadecene), demonstrating that both kerogen and HCs exchange hydrogen with water.

Giggenbach (1997) examined relative concentrations of CO_2 and CH_4 from three different geologic settings, and concluded that the gases were in chemical equilibrium both with each other and their environments, and had reached these equilibria via redox reactions with their host rocks. Graphite replaced by calcite in a gold–tungsten deposit at Macraes, New Zealand revealed that graphite had reduced the ore-bearing solution and was oxidized to carbon dioxide (McKeag et al., 1989). The expelled CO_2 gas lowers the pH of the surrounding formation waters, which promotes the development of secondary porosity and diagenetic reaction of detrital silicates to form authigenic mineral assemblages.

By the study of temperature–pressure conditions in coal bed methane reservoirs of the Black Warrior basin Pashin and McIntyre (2003) have recently shown that carbon sequestration and enhanced coal bed methane recovery show great promise in subcritical reservoirs.

Summary and conclusions

Therefore two main substances are produced in catastrophic events during coal mining - methane and carbon dioxide. Rapid formation of these products could be described by the direct reaction of coal and its organic matter with water on the mechanism of hydrolytic disproportionation of carbon (HDC). Water is a proposed source of the necessary amounts of hydrogen and oxygen for the reaction.

The calculated Gibbs free energy change of HDC or direct reduction of hydrogen from its oxide by coal in the form of carbon is 29.20 kJ/mol of methane or 14.60 kJ/mol of carbon. Reaction of methane formation from carbon and water is a slightly endothermic process, but the products entropy increases and the reaction is product-favored. Changes of the reaction entropy $\Delta S^\circ_{\text{rxn}} = 248.67 \text{ J/mol}\cdot\text{K}$ is positive and this reaction could be an “entropy driven”. Reaction energy could be compensated by the exothermic reaction of partial oxidation of methane in the conditions of exploitation of coal deposits.

The proposed mechanism of rapid methane formation by HDC is similar to processes which are observed under the hydrolytic disproportionation of organic matter (HDOM) in kerogens.

Methanogenesis by acetate fermentation is too slow in comparison with the rapid process of HDC methane formation during catastrophic events for which bacteria are not required.

There may be a possibility that the size and tetrahedral structure of methane molecules, similar to the stereochemistry of the holes of water clathrates, gives additional features of favorable stereochemistry during the formation of intermediate stereo-structures of hydrotated coal rings, acetic acid like dimers and polymers and their subsequent transformation and decomposition during HDC with the production of methane and carbon dioxide as the final substances; however, this speculation needs to be confirmed by future experimental observation.

Evaluation of the critical conditions of HDC shows that under the normal pressure Gibbs free energy becomes equal to zero under the temperatures of about 142°C which are characteristic for the depths of nearly 4 km. Conditions of mining and geological peculiarities could drastically change the situation during exploitation of coal deposits. CBM is kinetically controlled in a state that is far from equilibrium and in this situation catalysts and chain-type reactions on the free radical-mechanism could become important.

Disclaimer

The findings and conclusions in this paper are those of the author and do not necessary represents the views of the Institute of Comprehensive Exploitation of Mineral Resources, Russian Academy of Sciences.

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