Adsorption (2012) 18:189–198
DOI 10.1007/s10450-012-9393-3

Examination of sorption and desorption of hydrogen on several samples of polish hard coals

Janusz Cygankiewicz · Agnieszka Dudzińska · Mieczysław Żyła

Received: 26 August 2011 / Accepted: 8 June 2012 / Published online: 20 June 2012

Abstract Performed tests showed that at 298 K hard coals sorb relatively small amounts of hydrogen. Those amounts depend on carbon and oxygen content in tested coals. The most considerable amounts of hydrogen are sorbed by coals characterized by strong surface hydrophobicity and high content of aliphatic hydrocarbons. The hydrophilic nature of coal surface does not lead to higher sorption of hydrogen. It was found that the change in amount of sorbed hydrogen is closely related to the moisture. For high moisture coal a significant decrease in hydrogen sorption is observed. Also tests on hydrogen desorption on hard coals were carried out using method of lowering hydrogen pressure above the sorbent. Obtained results showed that tested coals desorb various amounts of hydrogen. Process of sorption is reversible only for some coals, while for the others the desorption isotherm partially lies beneath the sorption isotherm, which indicates that in addition to hydrogen some other chemical substances are emitted from coal.

Keywords Sorption · Hydrogen · Coal

1 Introduction

1.1 Hydrogen in mine air

The atmosphere in a coal mine contains hydrogen and its presence puts mines and working miners in danger. Results of particular chromatographic analyses made with use of a specialized gas chromatograph coupled with an add-on concentrating device enabling determination of hydrogen from as low a level as 0.5 ppm show that concentrations of hydrogen in mine air range from values in the order of ppm to the tenths of percent. In ventilated galleries and on wall inlets and outlets, concentration of hydrogen reaches the value from 0.5 to about 20 ppm. In gunis, wall bings and behind insulating dams it reaches values of hundreds of ppm. In case of fire hazard the level of hydrogen is much higher since hydrogen is a gas generated in the process of self-heating of coal. Together with progress of this process, hydrogen concentration increases. Above ignition temperature of coal significant amounts of hydrogen and carbon oxide are produced (van Heek and Hodek 1994). High concentration of hydrogen generated during fire occurs with high concentration of other fire gases: carbon oxide, ethene, propene and a decrease in content of oxygen (Lu et al. 2004). Dangerous situations are observed, when hydrogen concentration reaches values of several thousands of ppm, especially behind insulating dams but no endogenic fire takes place there and self-heating phenomenon is not detected. In air behind the dam low concentration of oxygen is then found and such a system does not constitute explosive mixture. Perhaps the emergence of those higher concentrations of hydrogen is related to some unknown phenomena.

1.2 Hydrogen adsorbed in the hard coal structure

As early as in 1975 authors of the study (Street et al. 1975) drew attention to the problem of hydrogen presence in freshly collected cobs. They were interested in emission of hydrogen which takes place when hard coal, prepared for combustion in coal power plants, is crushed. Based on observation, they noticed that there is a probability of explosion

J. Cygankiewicz · A. Dudzińska (✉)
Department of Mining Aerology, Central Institute of Mining, Plac Gwarków 1, 40-166 Katowice, Poland
e-mail: adudzinska@gig.katowice.pl

M. Żyła
Fuel and Energy Departament, Academy of Metalurgy and Mining, Al. Mickiewicza 30, 30-047 Kraków, Poland

of emitted hydrogen, which when mixed with oxygen forms a dangerous explosive mixture. In further research it was found out that amounts of generated hydrogen increase with a temperature growth when time of coal crushing elapses. Probably emitted hydrogen resulted from desorption taking place during the process of crushing hard coal cobs. It was also revealed that time of coal heating up affects the amount of desorbed hydrogen. It was also assumed that hydrogen in hard coal is the product of reaction of warm carbon with water vapour:

$$C + H_2O \rightarrow CO + H_2$$

Possibility of disintegration of hydrocarbons present in hard coal was also considered according to reaction:

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2$$

Problem of hydrogen in contact with coal has also been the subject of research of authors Davidi et al. (1995), Grossman et al. (1994). They performed tests on American and Australian coals and their studies showed that low-temperature coal oxidation is the source of hydrogen and they observed hydrogen emission already at 313 K. They concluded that amounts of emitted hydrogen depend on time of coal oxidation, temperature of the process and slightly on mass of the processed coal. The higher temperature and longer time of oxidation, the bigger amounts of emitted hydrogen. In their research they did not find any correlation between moisture present in coal or degree of coal crushing and amount of emitted hydrogen. They proved that amount of produced hydrogen is linearly correlated with amounts of oxygen utilized in oxidation process. However type of tested coal, oxidation degree and content of ash have minor influence on hydrogen generation. The authors supposed that hydrogen can be sorbed inside the coal pores, but this amount is small in comparison to emission of hydrogen to the atmosphere. According to other scientists (Nehemia et al. 1999) hydrogen emitted in the process of coal oxidation is generated as a result of decomposition of formaldehyde, which is an intermediate product formed in the reaction of coal oxidation. In addition to hydrogen during formaldehyde degradation carbon dioxide is also formed. Carbon is considered to be a catalyst of this reaction.

By studies of Marzec and Czajkowska (2005), Marzec (2006) hydrogen is generated as a result of oxidation of polish hard coals. In their experiment hydrogen emerges just after 48 h of oxidation at 323 K. Prior to oxidation no hydrogen emission from coal in desorption process was observed. There is an assumption that hydrogen is formed very quickly simultaneously with carbon oxides, at the initial stage of generation of gaseous products already.

It is also thought that hydrogen is formed due to low-temperature oxidation of tested coals and is a result of reaction between oxygen and unsaturated double bonds in chain and alicyclic carbon configurations. As products of these reactions aldehyde groups are formed, which react with water vapour to give hydrogen and structures containing a carboxylic group. An amount of hydrogen formed is similar for all tested coals. Hydrogen can accumulate in upper parts of space e.g. in mine galleries with poorer ventilation as well as in waste banks. It is known that local accumulation of hydrogen can lead to dangerous concentrations threatening with explosion.

The hard coal is a complex system of many aromatic, aliphatic and alicyclic compounds formed during geochemical transformations of organic substances present in plants (Clarkson and Bustin 1999). The basic structure of hard coal is an organic polymer made of aromatic rings with aliphatic hydrocarbons on their edges. Sorption of vapours and gases conducted on hard coals is a source of much information concerning mainly polarity, surface and porosity of coals, which are used to describe their properties. Many papers have been published in the ares of gases sorption such as carbon dioxide, methane, water, carbon monoxide, hydrocarbons (Chaback et al. 1996; Krooss et al. 2002; Prusty 2008; Prinz and Littke 2005). The most attention was focused on sorption of carbon dioxide and methane (Mastalerz et al. 2004; Larsen 2004; Ceglarska-Stefańska and Zarębska 2005; Siemons and Busch 2007; Ottiger et al. 2008).

Research works regarding sorption of hydrogen on hard coal samples are rarely carried out in experimental laboratories while examination of hydrogen sorption on activated carbon is well known. Experiments were conducted at 77 K in pressure range up to 760 mm Hg by measuring sorption on hard coals and activated carbons derived from them (Kopac and Toprak 2009). Many time larger capacity of hydrogen sorption on activated carbons than on hard coals was observed. Problem of hydrogen sorption on active carbon has also been the subject of research of authors Nijkamp et al. (2001), Buczek et al. (2005).

The purpose of this paper is to examine sorption of hydrogen on hard coals and to determine if hard coals samples sorb hydrogen at room temperature in a measurable way, if sorption of hydrogen depends on the type of coal and finally, if nature of the process of hydrogen sorption is reversible. In this paper the examination of sorption and desorption of hydrogen on selected hard coals is presented. The selection of particular coals was based on different oxygen content, moisture content and various porosity of those coals.

2 Experimental

2.1 Determination of sorption isotherms of hydrogen

Laboratory tests on sorption of hydrogen were carried out on 9 samples of hard coals of varied degrees of metamorphism collected from active Polish coal mines. Prior to measurement coal samples were crushed to grain size ranging from 0.5 to 0.7 mm, flushed with helium and then degassed to a vacuum of about $5.06 \cdot 10^{-7}$ Pa.

Chemical and petrographic properties of the hard coals tested are listed in Table 1. Data on the porosity and the pore volumes are contained in Table 2. Tests of sorption were performed using volumetric method, at 298 K and in range of low pressures up to 0.09 MPa, applying a modern, fully automated apparatus ASAP 2010 made by Micromeritics. This apparatus enables determination of sorption and desorption isotherms on granulated and powdered samples with use of various sorption gases, among them hydrogen. The obtained hydrogen sorption isotherms are shown in Fig. 1. The amounts of sorbed hydrogen are small, with maximal value of about 0.18 cm^3/g. The isotherms feature linear shapes with slight deviation at higher pressures. Analyzing the shape of isotherms presented in Fig. 1, it can be stated that the obtained isotherms can be divided into 3 groups corresponding to the varied amount of sorbed hydrogen. The biggest amount of hydrogen is sorbed in the case of coal from Wesoła mine. The content of carbon in this coal is 79.46 % and is analogous to the content of carbon in other coals, which sorb smaller amounts of hydrogen, e.g. Chwałowice (79.29 %), Halemba (79.02 %) or Zofiówka (78.62 %). The total porosity and pore volume were determined based on the results of porosimetric measurements for coal from Wesoła Mine and are respectively (3.87 %; 28.85 mm^3/g), which is comparable with values obtained for other coals tested. The elevated hydrogen sorption of coal from Wesoła mine can probably be attributed to its high content of inertinite. The other samples of coals tested sorb smaller amounts of hydrogen. The coals from the following mines: Chwałowice (79.29 % C), Bobrek (77.12 % C), Sośnica (70.82 % C) feature similar sorption of hydrogen of about 0.15 (cm^3/g). The total porosity of this group of coals varies from 2.37 % for coal from Sośnica Mine to 4.05 % for coal from Bobrek Mine. The coals of the third group characterized by the weakest sorption ability of hydrogen come from mines: Pniówek (84.24 % C), Halemba (79.02 % C), Zofiówka (78.62 % C) and Jaworzno 209 and 207 (57.83 % C, 66.51 % C). Coals which sorb the lowest amounts of hydrogen demonstrate a diverse degree of porosity—from low values for coals from mines: Pniówek, Zofiówka (2.81 %; 2.39 %) to the highest values for coals from Jaworzno Mine (8.7 %; 13.55 %). The significant pore volumes of those coals do not conduce to higher sorption of hydrogen, either. The increase in porosity of hard coals does not favour the higher hydrogen sorption. It is likely that there are other factors which, to a much higher degree, determine the behavior of a given coal with reference to sorbed hydrogen. Coals with considerable values of the total porosity are considered to be good sorbents, e.g. coals from Jaworzno Mine, demonstrate limited sorption of hydrogen.

It is commonly known that the degree of metamorphism has a significant influence on sorption of gases on hard coals. This thesis has been confirmed by numerous studies concerning sorption of water, carbon dioxide or methane (Mahajan 1991; Levy et al. 1997; Bustin and Clarkson 1998). Relation between amount of sorbed gas and the degree of metamorphism for hydrogen sorption is shown in Fig. 2. In the range of carbon content of 55–73 % C tested coal samples showed systematic growth of amounts of sorbed hydrogen. Starting with a sample containing 73 % C the sorption of hydrogen decreases. The maximum of sorbed hydrogen falls on hard coals with a carbon content of 70–80 %. Hard coals containing of 55–73 % of carbon possess on their hydrophobic surface numerous groups containing oxygen such as carboxyl, hydroxyl and carbonyl groups, responsible for wettable (hydrophilic) character of coal surface. These coals sorb relatively small amounts of hydrogen. In the case of coals containing from 70 to 80 % of carbon, characterized by highest amounts of sorbed hydrogen, their structure is rich in aliphatic and alicyclic hydrocarbons which develop hydrophobic character of those coal samples. This is the case of "coking" coals. Most likely there is a dispersive interaction between hydrophobic areas on coal surface and hydrogen molecules. Other coal samples containing more than 80 % C are only slightly wettable. These coals consist of condensed benzene rings containing the sextet of mobile electrons. It is probable that π electrons, orbiting in benzene rings, are the reason for creating oscillatory dipoles. These dipoles are responsible for the specific polarity of the condensed configuration of aromatic hydrocarbons, which leads to a decrease in the amount of sorbed hydrogen. The performed laboratory tests (Fig. 2) showed that only the coals with hydrophobic surface sorb hydrogen molecules well. The process of sorption takes place in consequence of dispersive interaction forces between hydrogen molecules and the nonpolar areas of the hard coal surface.

Performed laboratory tests also showed that amounts of hydrogen sorbed are related to the percentage of oxygen in hard coal. Figure 3 presents an influence of amount of oxygen on sorption of hydrogen. Marked in Fig. 3 are two curves related to two groups of coals, which differ considerably in terms of amount of sorbed hydrogen but the maximum of hydrogen sorption is in the same range of oxygen content of 6–8 %. Samples from five mines show higher hydrogen sorption ability (curve 1) than four samples collected from other mines despite the same percentage of oxygen (curve 2). Curves describing the amount of sorbed hydrogen as a function of oxygen content (Fig. 3) confirm conclusions resulting from the shape of correlation between the amount of sorbed hydrogen and content of carbon. Coals of medium oxygen content showing hydrophobic character of surface demonstrate maximal amounts of sorbed hydrogen. Moisture content in coals also plays a significant

Table 1 Chemical and petrographic characteristics of coal samples

Properties	Symbol	Unit	Samples from the following mines								
			Pniówek s. 360	Wesoła s. 501	Chwałowice s. 404	Zofiówka s. 404/2	Sośnica s. 413	Jaworzno s. 209	Halemba s. 506	Bobrek s. 507	Jaworzno s. 207
carbon	$C_t{}^a$	%	84.24	79.46	79.29	78.62	70.82	57.83	79.02	77.12	66.51
sulphur total	$S_t{}^a$	%	0.39	0.32	0.35	0.35	3.50	1.10	0.90	0.54	0.89
sulphur from pyrite	$S_p{}^a$	%	0.01	0.07	0.16	0.01	3.20	0.71	0.42	0.22	0.61
hydrogen	$H_t{}^a$	%	4.58	4.55	4.97	4.37	3.35	3.37	4.81	4.70	3.93
nitrogen	N^a	%	1.52	1.27	1.07	1.15	1.28	0.87	1.13	0.89	0.91
sulphur from ash	$S_A{}^a$	%	0.07	0.22	0.19	0.18	1.27	0.03	0.45	0.25	0.17
sulphur combustible	$S_c{}^a$	%	0.32	0.10	0.16	0.17	2.23	1.07	0.45	0.29	0.72
oxygen (calculated)	$O_d{}^a$	%	4.58	8.07	8.47	6.17	6.29	11.30	8.29	9.69	11.63
moisture	W^a	%	1.75	3.69	3.39	0.60	1.85	11.11	2.57	3.08	13.95
ash	A^a	%	3.01	2.86	2.65	8.92	14.18	14.45	3.73	4.23	2.35
volatile matter	V^a	%	27.12	30.40	35.62	27.93	29.88	28.39	29.86	31.80	29.73
vitrinite	V_t	% obj	73	38	60	91	60	67	40	59	66
reflexivity of vitrinite	R_0	%	0.92	0.72	0.70	1.01	0.78	0.51	0.69	0.71	0.52
liptinite (exinite)	L	% obj	7	9	10	1	9	5	7	8	6
inertinite	I	% obj	20	53	30	8	31	28	27	36	27
mineral substance	M	% obj	1	2	1	4	14	11	2	3	2

Table 2 Total porosity and pore volumes of coals samples

Samples from the following mines	Total porosity, %	Pore volume, mm^3/g
Pniówek s. 360	2.81	21.80
Wesoła s. 501	3.87	28.85
Chwałowice s. 404	3.47	27.98
Zofiówka 404/2	2.39	18.37
Sośnica s. 413	2.37	18.18
Jaworzno s. 209	13.55	115.44
Halemba s. 506	5.47	41.6
Bobrek s. 507	4.05	30.9
Jaworzno s. 207	8.7	68.6

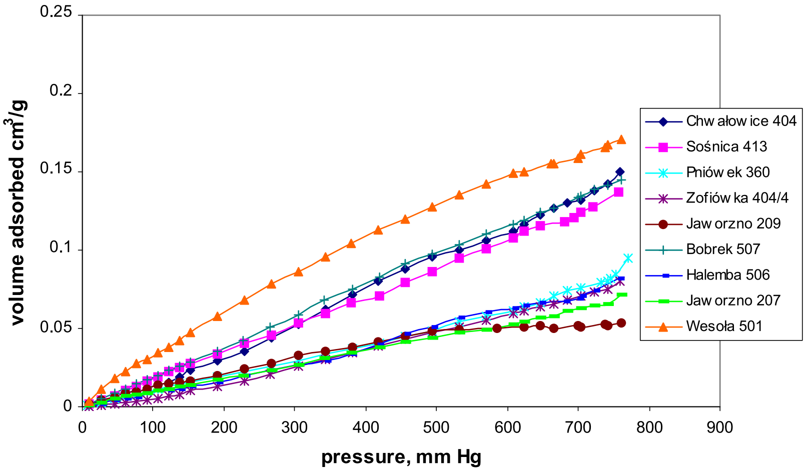


Fig. 1 Isotherms of hydrogen sorption at 298 K on coals samples of different coals of 0.5–0.7 mm particle size

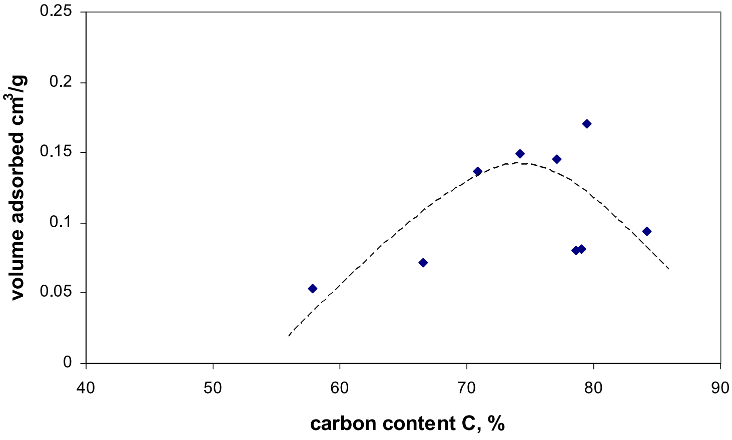


Fig. 2 Relation between volume of hydrogen adsorbed at 298 K and carbon content in coal samples

role in the process of sorption. Relation between amounts of sorbed hydrogen and content of moisture is shown in Fig. 4. When moisture content is in the range of 0.5–4 %, amount of sorbed hydrogen clearly rises, while for the range of 4–14 % it drops significantly. Based on the shape of the graph it can be assumed that little amount of water does not hinder hydrogen molecules from sorption but considerable increase in number of water molecules in coal structure is a serious obstacle in interaction between hydrogen molecules and centers to which they should be bonded. On this basis it can be concluded that substantial moisture of hard coal can prevent the sorption of hydrogen on hard coals. Additionally, introducing big amounts of water to coal can cause desorption of previously sorbed hydrogen. Interesting is the influence of the percentage of petrographic components of tested coals on sorption of hydrogen. Coal samples containing great amount of inertinite sorb respectively significant volumes of hydrogen. As an example can serve coal sam-

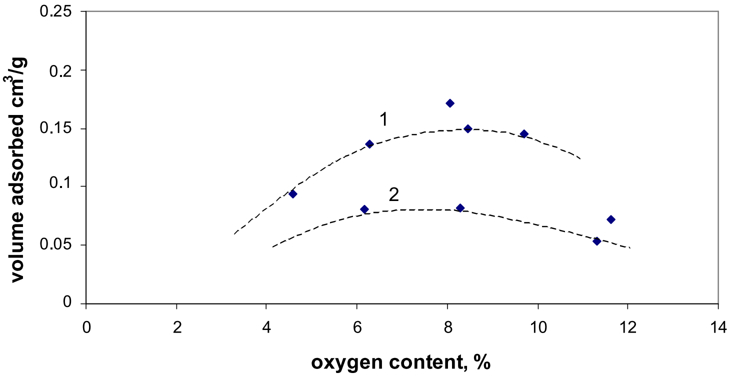


Fig. 3 Relation between volume of hydrogen adsorbed at 298 K and oxygen content in coal samples

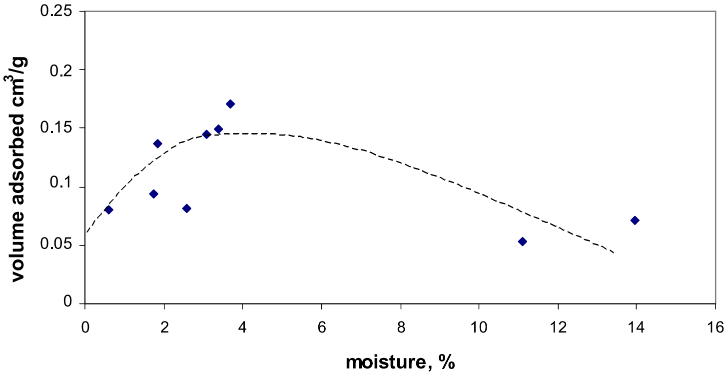


Fig. 4 Relation between volume of hydrogen adsorbed at 298 K and moisture in coal samples

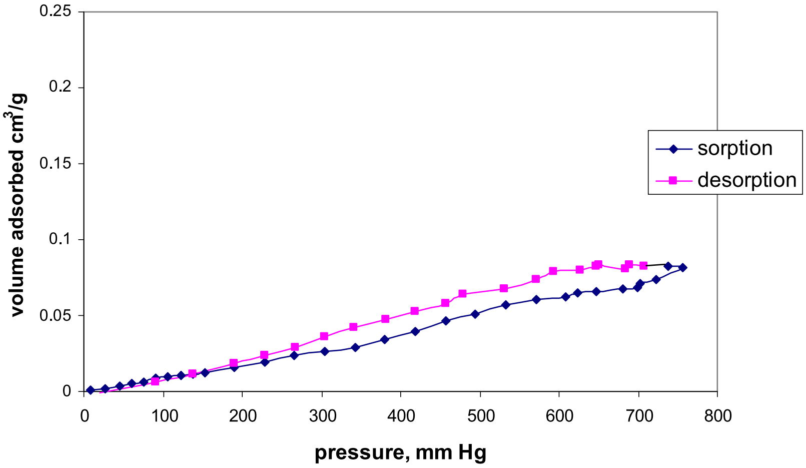


Fig. 5 Isotherms of sorption and desorption of hydrogen in Halemba mine sample determined at 298 K

ples collected from mines: Wesoła, Chwałowice, Bobrek and Sośnica.

2.2 Desorption of hydrogen from hard coals

Sometimes there is an elevated content of hydrogen in mine air. The considerable share of amount of this gas can be probably attributed to the process of coal self-heating. However, there is a probability that some part of hydrogen in mine air comes from desorption of previously sorbed hydrogen. To check if hard coal tends to retain hydrogen in its structure the tests on desorption of previously sorbed hydrogen were performed at the same temperature as for sorption tests (298 K), using method of lowering pressure above the sample. The hydrogen sorption and desorption isotherms for particular hard coals are compared in Figs. 5–13.

Analyzing the shape of desorption isotherms it can be noticed that only in the case of the several samples of hard coals the process of sorption is almost completely reversible. Desorption and sorption isotherms converge and form closed hysteresis loop (Figs. 5, 6, 7). For the next three coals desorption is only partly reversible. The desorption isotherm with values of pressure 300–400 mm Hg lies partially under the sorption isotherm (Figs. 8, 9, 10). For the next three samples of hard coals collected from mines: We-

Fig. 6 Isotherms of sorption and desorption of hydrogen in Pniówek mine sample determined at 298 K

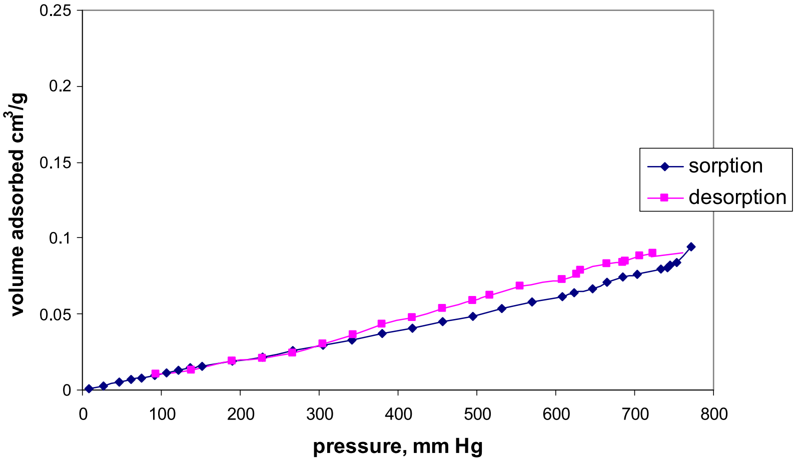


Fig. 7 Isotherms of sorption and desorption of hydrogen in Zofiówka mine sample determined at 298 K

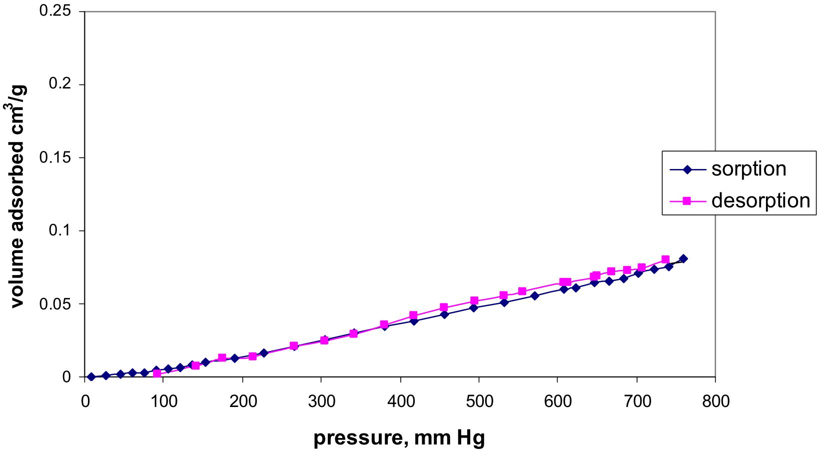
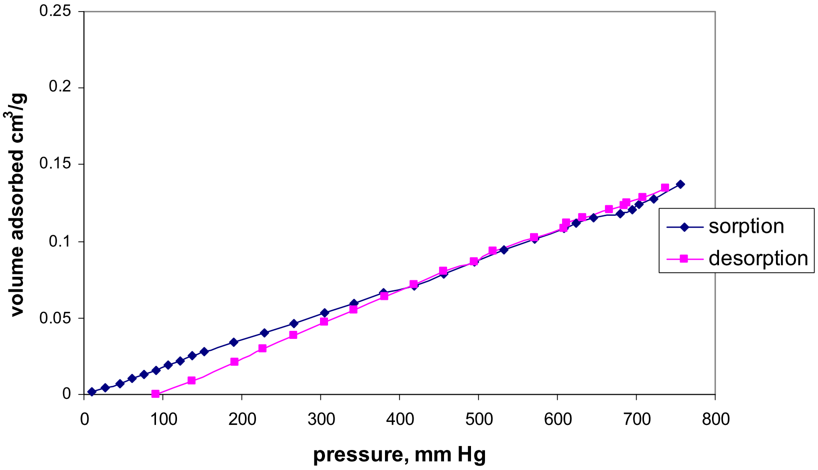


Fig. 8 Isotherms of sorption and desorption of hydrogen in Sośnica mine sample determined at 298 K



soła, Bobrek, Jaworzno hydrogen sorption features “negative” nature. Desorption isotherms in all pressure range lie beneath sorption isotherms. It indicates that those coals desorb larger amounts of gas than the volumes of sorbed hydrogen (Figs. 11, 12, 13). According to the model of the chemical structure of coal put forward by Shinn (1984) oxygen in coal forms the following reactive groups: (hydroxyl, carboxyl, carbonyl). There is also nonreactive oxygen in coal, which can react with the sorbed hydrogen giving gaseous compounds. The bonding between hydrogen and the oxygen groups is energy-rich and probably hydrogen can desorb under reduced pressure in the adsorptive system. This hydrogen, emitted in statu nascendi, can be highly explosive.

Fig. 9 Isotherms of sorption and desorption of hydrogen in Chwałowice mine sample determined at 298 K

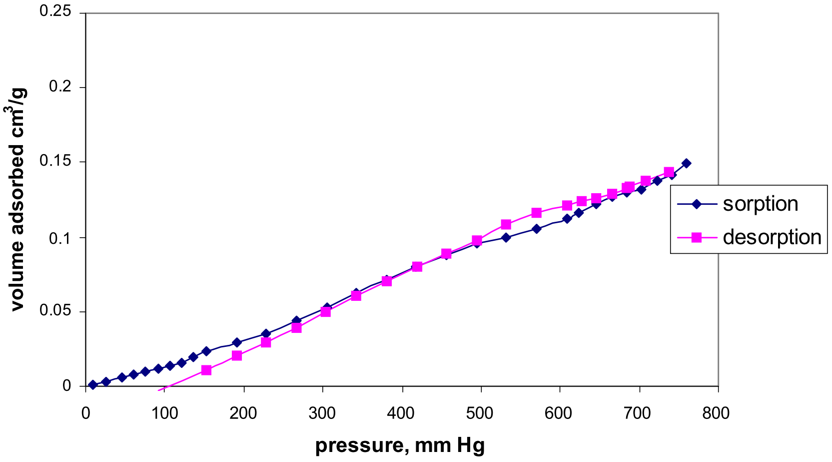


Fig. 10 Isotherms of sorption and desorption of hydrogen in Jaworzno 207 mine sample determined at 298 K

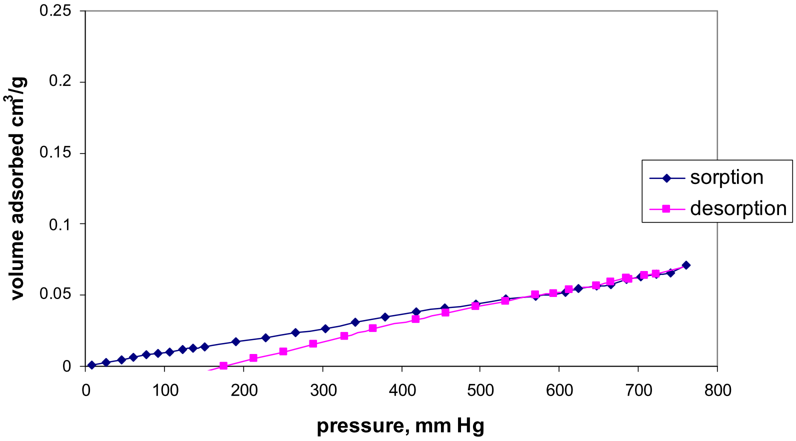
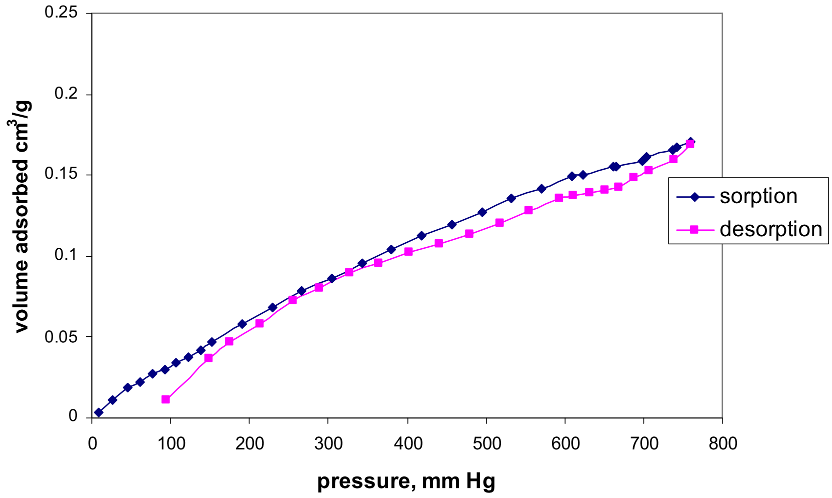


Fig. 11 Isotherms of sorption and desorption of hydrogen in Wesoła mine sample determined at 298 K



Interesting phenomenon presents a relatively small amount of sorbed hydrogen on coals collected from 209 and 207 coal seams in Jaworzno mine. These coals despite of big total amount of oxygen (11.3 %; 11.63 %) sorb only limited amounts of hydrogen. It is probably caused by “horizontal” energetic interactions between particular oxygen groups of coal leading to the formation of oxygen complexes. The set of energetically connected two or more oxygen groups can adsorb only a single hydrogen molecule.

3 Conclusions

Hard coals sorb only small amounts of hydrogen at 298 K. The hydrogen sorption depends on the percentage of carbon.

Fig. 12 Isotherms of sorption and desorption of hydrogen in Jaworzno 209 mine sample determined at 298 K

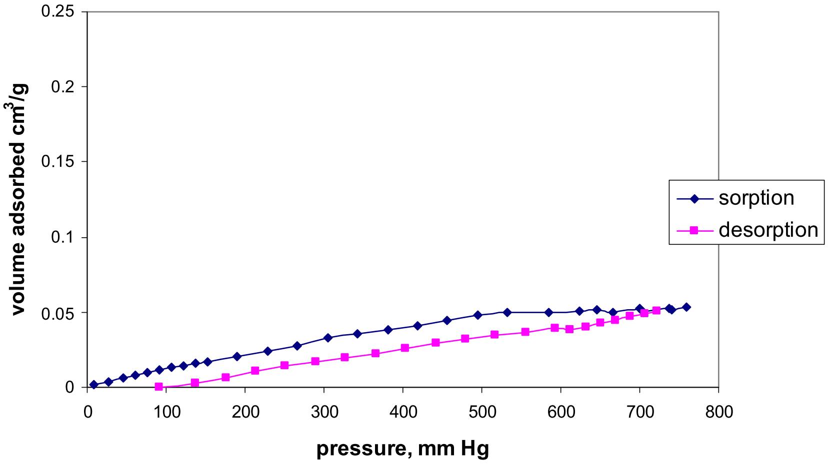
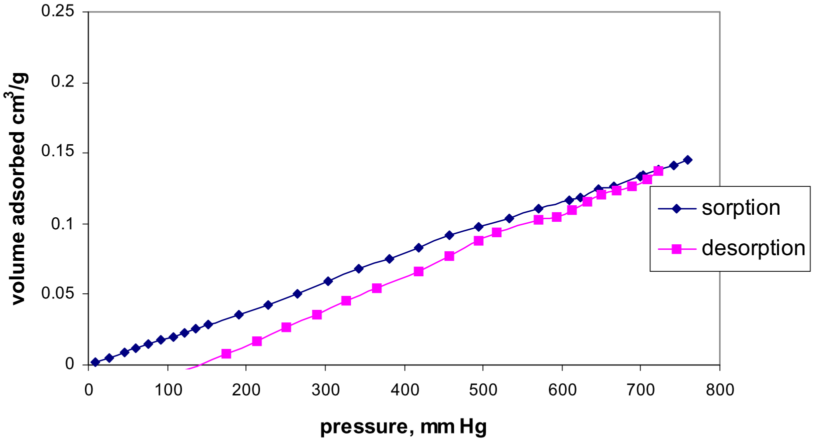


Fig. 13 Isotherms of sorption and desorption of hydrogen in Bobrek mine sample determined at 298 K



The most considerable amounts of hydrogen are sorbed by coals containing 70–80 % of carbon. Sorption of hydrogen depends also on the percentage of oxygen. With the increase in oxygen content the sorption of hydrogen goes up and then slowly falls. Analysing the correlation between amounts of sorbed hydrogen and content of carbon and oxygen it can be assumed that hydrogen is sorbed mainly on the hydrophobic centers of coal surfaces. The fact remains, however, that hydrophilic nature of hard coal surface does not favour sorption of hydrogen. The total porosity shows no major impact on amounts of sorbed hydrogen. Highly porous coals sorb limited amounts of hydrogen.

Correlation between moisture contained in coals and hydrogen sorption is also an interesting aspect. The values of hydrogen sorption increase in the range of 1–4 % of moisture and then drop significantly for coals containing of about 12 % moisture. Probably oxygen groups present in hard coals are thought to hamper sorption of hydrogen on polar areas of coal surface. Process of hydrogen desorption is reversible only on a few coal samples. In the case of the others the desorption isotherm lies beneath the sorption isotherm, which indicates that in addition to hydrogen some other chemical substances are emitted from coal.

References

Buczek, B., Czepirski, L., Ziętkiewicz, J.: Improvement of hydrogen storage capacity for active carbon. Adsorption **11**, 877–880 (2005)

Bustin, R.M., Clarkson, C.R.: Geological controls on coalbed methane reservoir capacity and gas content. Int. J. Coal Geol. **38**, 3–26 (1998)

Ceglarska-Stefańska, G., Zarębska, K.: Sorption of carbon dioxide-methane mixtures. Int. J. Coal Geol. **62**, 211–222 (2005)

Chaback, J.J., Morgan, W.D., Yee, D.: Sorption of nitrogen, methane, carbon dioxide and their mixtures on bituminous coals at in-situ conditions. Fluid Phase Equilib. **117**, 289–296 (1996)

Clarkson, C.R., Bustin, R.M.: The effect of pore structure and gas pressure upon the transport properties of coal: a laboratory and modeling study. 1. Isotherms and pore volume distributions. Fuel **78**, 1333–1344 (1999)

Davidi, S., Grossman, S.L., Cohen, H.: Organic volatiles emissions accompanying the low-temperature atmospheric storage of bituminous coals. Fuel **74**, 1357–1362 (1995)

Grossman, S.L., Davidi, S., Cohen, H.: Emission of toxic and fire hazardous gases from open air coal stockpiles. Fuel **73**, 1184 (1994)

Kopac, T., Toprak, A.: Hydrogen sorption characteristics of Zonguldak region coal activated by physical and chemical methods. Korean J. Chem. Eng. **26**(6), 1700–1705 (2009)

Krooss, B.M., van Bergenb, F., Gensterbluma, Y., Siemonsa, N., Pagnierb, H.J.M., Davidb, P.: High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals. Int. J. Coal Geol. **51**, 69–92 (2002)

Larsen, J.W.: The effects of dissolved CO_2 on coal structure and properties. Int. J. Coal Geol. **57**, 63–70 (2004)

Levy, J.H., Stuart, J.D., Killingley, J.S.: Methane capacities of Bowen Basin coals related to coal properties. Fuel **76**(9), 813–819 (1997)

Lu, P., Liao, G.X., Sun, J.H., Li, P.D.: Experimental research on index gas of the coal spontaneous at low-temperature stage. J. Loss Prev. Process. Ind. **17**, 243–247 (2004)

Mahajan, O.P.: CO_2 surface area of coals: the 25-year paradox. Carbon **29**, 735–742 (1991)

Marzec, A., Czajkowska, S.: Molecular hydrogen generation as a consequence of atmospheric oxidation of coals. In: Proceedings of the 10th Session of Intern. Bureau of Mining Thermophysics, Gliwice, February, pp. 51–56 (2005)

Marzec, A.: Coalmine hydrogen. In: Proceedings of the Workshop on Coalmine and Coalbed Methane. UN Economic Commission for Europe. St. Petersburg, 20–22 Sept. (2006)

Mastalerz, M., Gluskoter, H., Rupp, J.: Carbon dioxide and methane sorption in high volatile bituminous coals from Indiana, USA. Int. J. Coal Geol. **60**(1), 43–55 (2004)

Nehemia, V., Davidi, S., Cohen, H.: Emission of hydrogen gas from weathered steam coal piles via formaldehyde as a precursor. Fuel **78**, 775–780 (1999)

Nijkamp, M.G., Raaymakers, J.E.M.J., van Dillen, A.J., de Jong, K.P.: Hydrogen storage using physisorption-materials demands. Appl. Phys. **72**, 619–623 (2001)

Ottiger, S., Pini, R., Storti, G., Mazzotti, M.: Competitive adsorption equilibria of CO_2 and CH_4 on dry coal. Adsorption **14**, 539–556 (2008)

Prinz, D., Littke, R.: Development of the micro- and ultramicroporous structure of coals with rank as deduced from the accessibility to water. Fuel **84**, 1645–1652 (2005)

Prusty, B.K.: Sorption of methane and CO_2 for enhanced coalbed methane recovery and carbon dioxide sequestration. J. Nat. Gas Chem. **17**, 29–38 (2008)

Siemons, N., Busch, A.: Measurement and interpretation of supercritical CO_2 sorption on various coals. Int. J. Coal Geol. **69**, 229–242 (2007)

Shinn, J.H.: From coal to simple-stage and two stage products; a reactive model of coal structure. Fuel **63**, 1187–1196 (1984)

Street, P.J., Smalley, J., Cannigham, A.T.S.: Hydrogen as an indicator of the spontaneous combustion of coal. Journal of the Insitute of Fuel **48**, 146–152 (1975)

van Heek, K.H., Hodek, W.: Structure and pyrolysis behaviour or different coals relevant model substances. Fuel **73**(6), 886 (1994)