



Sorption of CO₂ in lignites from Polish coal mines: measurements and thermodynamic analysis

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Abstract The purpose of the work presented in this paper was to adapt the Multiple Sorption Model (MSM), originally developed for hard coals, to study sorption in lignites. It also includes an analysis of the sorption process of small molecule compounds in lignites. Measurements were made of the sorption isotherms of carbon dioxide in two samples of lignite from Polish collieries at different temperatures (298, 313 and 323 K) and in the pressure range up to 5 MPa. Subsequently, simulations of the isotherms for selected carbon dioxide-lignite systems were performed using the MSM. They were evaluated using the empirical isotherms until agreement of the isotherms was attained and the parameters of the sorption system reached reasonable values. Surprisingly, a low contribution of absorption was found in the overall sorption process probably as an effect of the high porosity of the sample and the presence of a large number of high-energy sites on the coal surface. Sorbate molecules occupied these high-energy sites on the surface and did not migrate to the absorption subsystem.

Keywords Lignite · Sorption · Adsorption · Absorption · Expansion · Carbon dioxide · Modelling

1 Introduction

Greenhouse gases are nowadays a topic of special interest. Many ideas have emerged for the utilisation of carbon dioxide and the most important of these is geological sequestration, one concept for which includes the possibility of CO₂ sorption in the coal bed, especially in those deposits, which are not considered to be capable of exploitation on technical grounds. (Haljasmaa et al. 2011) Lignites are lightly metamorphosed natural carbonaceous materials and generally are located near the surface of the earth. In comparison with sub-bituminous coal, lignites are substances of high porosity, so it is easy for carbon dioxide to pass through their structure (Firouzi and Wilcox 2012). This excludes the possibility of carbon dioxide storage; nevertheless studies of carbon dioxide sorption in lignites are interesting from the scientific point of view. The possibility of using of lignite for the sequestration of carbon dioxide has neither been confirmed nor denied. In the literature there are studies presented that demonstrate that storage of carbon dioxide is possible due to the high sorption of carbon dioxide and self-sealing of the bed, and contradictory studies that show that leakage from the bed can lead to the release of this gas into the atmosphere. Therefore, this issue requires further study to clarify the nature of the phenomenon. Studies that confirm the self-sealing nature of the bed due to swelling of the coal mass can demonstrate the possibility of using deposits of lignite for the sequestration of CO₂. The measurements and theoretical analysis presented are voices in the discussion on the application of methods for the storage of carbon dioxide in lignites. Our investigations also are focused on the extension and application of the Multiple Sorption Model (MSM) for lignites because it was originally developed for hard coals (Jodlowski and Wojcik 2013). A

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spectrum of phenomena which play a role in the sorption of gas in the lignite structure are taken into account. The model examined adsorption in the porous system and the expansion of submicropores, in addition to absorption. The swelling and contraction of the pores are phenomena accompanying absorption and expansion, which affects adsorption and the movement of molecules of carbon dioxide in a bulk deposit of coal. Thus, swelling and contraction cause the immobilization of CO₂ molecules in the structure. Demonstrating that carbon dioxide sequestration in deposits of lignite is possible is the indirect object of this work.

The MSM is a tool for the estimation of the parameters of a sorption system such as factors describing of the structure of coal (submicropore distribution as well as the distribution of larger pores); the energy properties of the coal surface and its interaction with sorbate molecules; interactions of the sorbate molecules between subsystems, and the distribution of sorbate among the subsystems. This is a development of Flory polymer solution theory (Flory 1953) taking into account the complex co-polymeric composition of coal extended with a model of multilayer adsorption of the adsorbate molecules with limitations of the layer capacity (expanded BET-like model). The model allows to divide sorption phenomena on three main subsystems: adsorption, absorption and expansion.

Determination of the participation of absorption and expansion in the total sorption and the energy of these phenomena can test the hypothesis of possibility of carbon dioxide storage in the bed of lignite.

2 Measurements

Two samples of lignites from Polish collieries (the Bełchatów—Be sample and the Turów—Tu sample) were investigated. Simplified results from ultimate and proximate analysis, and porosimetry measurement are presented in Table 1. A more detailed description is presented in the paper written by Macuda et al. (2011). Analysis of low-pressure sorption isotherms of CO₂ on presented samples is given in the article written by Baran et al. (2014).

Measurements were made of the sorption isotherms of carbon dioxide at three different temperatures (298, 313 and 323 K) in the pressure range up to 5 MPa in the installation presented schematically in Fig. 1.

Sorption isotherms were measured using volumetric apparatus applying the manometric method. High-pressure gas is decompressed from the reference cell (dosing space) with a specified pressure and volume to the sample cell containing a coal sample. Pressure measurements were conducted with a pressure transducer S-10 (WIKA)

Table 1 Selected parameters of coal samples

| Parameter | Sample | |
|---|--------|-------|
| | Tu | Be |
| C ^{daf} (%) | 70.2 | 65.9 |
| H ^{daf} (%) | 6.00 | 5.78 |
| N ^{daf} (%) | 0.7 | 0.81 |
| O ^{daf} (%) | 22.66 | 25.97 |
| V ^{daf} (%) | 54.06 | 57.39 |
| A ^a (%) | 12.3 | 3.8 |
| W ^a (%) | 8.3 | 21.1 |
| ρ_{He} (g/cm ³) | 1.45 | 1.43 |
| ρ_{Hg} (g/cm ³) | 1.25 | 1.04 |
| $V_{macro} \times 10^2$ (cm ³ /g) | 10.67 | 26.09 |
| $(V_{micro} + V_{meso}) \times 10^2$ (cm ³ /g) | 0.47 | 0.13 |

Index *daf* Ash free and dry conditions; Index *a* analytic state (for A ash and W moisture); ρ_{He} helium density, ρ_{Hg} mercury density, V_{micro} volume of micropores, V_{meso} volume of mesopores, V_{macro} volume of macropores

operating in the range 0–100 bar and the accuracy level falls in the class 0.25 % BSFL (Best Fit Straight Line). A high accuracy of pressure measurements is very important because the precision of the evaluation of the amount sorbed depends on having the correct pressure readings. The main parts of the apparatus reference cell, the dosing unit and sample cell, are sunk in the isothermal box which preserves the thermal stability of the measurement, and the TC Pt 100 temperature recorder controls this with an accuracy of 0.1 K.

The measurement schedule contains the following steps: i. Degassing of the measurement space with a coal sample (V1 and V2 valves are open—Fig. 1); ii. Filling the reference cell (V1 closed); iii. Feeding the sample cell (V2 closed, V1 open); iv. Reaching an equilibrium in the sample cell; v. Refilling the reference cell (V1 closed, V2 open). Constant pressure in the sample cell under the fourth step is the criterion for reaching equilibrium, thus this point of the schedule is the most time-consuming. Sorption equilibrium is reached if constant pressure in the sample cell is maintained for 72 h. The procedure from point i. to iv. is repeated until the maximum pressure is reached. The sorbed amount of the gas is calculated on the basis of the pressure difference before (point iii) and after sorption (point iv) taking into account the so-called dead space (volume of the apparatus after subtraction of the sample volume) or void volume (Dutta et al. 2008). The amount of gas recalculated in standard volume (at standard temperature and pressure: $p = 0.1$ MPa, $T = 298.2$ K) per mass of coal unit at the actual pressure and temperature is calculated from Eq. 1:

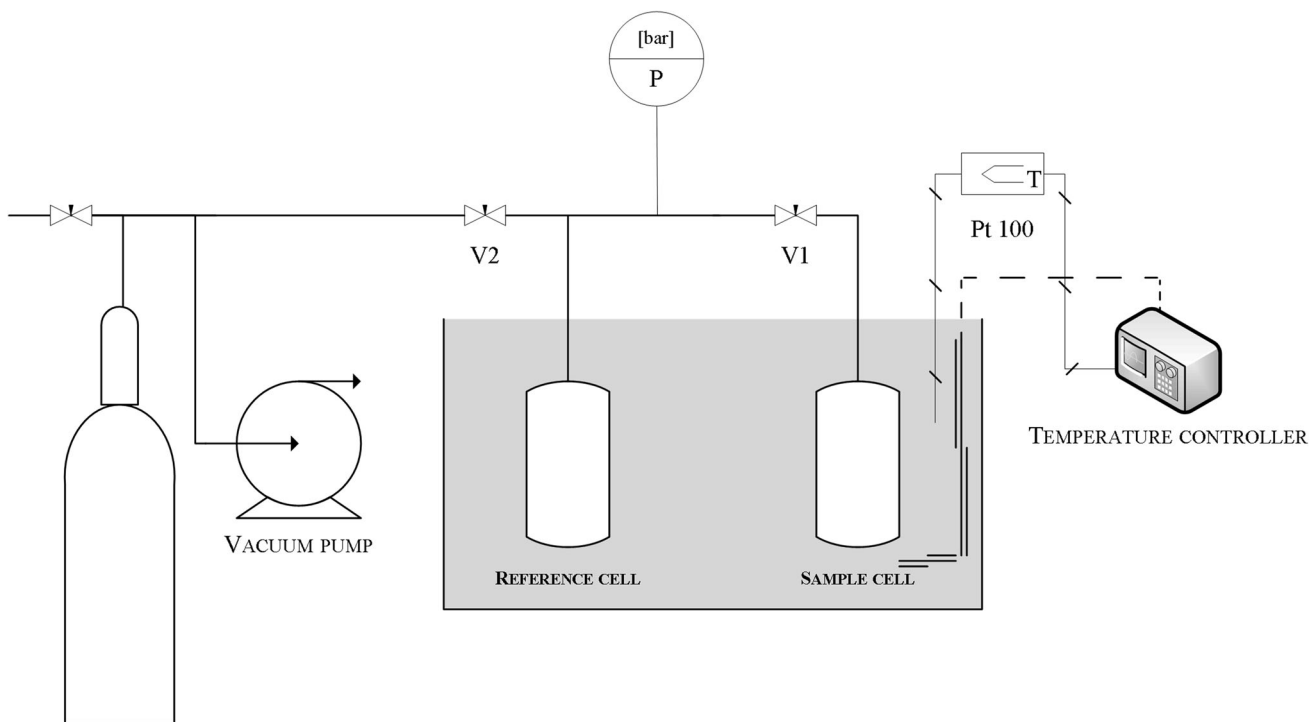


Fig. 1 Schematic diagram of the high-pressure installation for the measurement of carbon dioxide isotherms

$$V_p^T = \left[V_n^s - \frac{V_{mol}^n}{V_{mol}} \cdot V_{ap} \right] \cdot \frac{1}{m} \tag{1}$$

where V_n^s is the volume of gas introduced to the cell at the specified pressure of sorption, re-calculated under standard conditions (dm^3); V_{mol}^n is the molar volume of gas under standard conditions (dm^3/mol); V_{mol} is the molar volume of gas calculated for the currently measured pressure and temperature inside the cell (dm^3/mol), V_{ap} means the void volume of the sample cell (dm^3) and m is the coal mass (kg).

Carbon dioxide exhibits divergence from the ideal gas properties so it is necessary to take into account the corrections included using the Span-Wagner equation of state (Span and Wagner 1996).

Samples of coal were prepared with grain sizes 0.5–1.5 mm and they were degassed for 24 h at the experiment temperature in a 10^{-3} Pa vacuum before measurements were taken.

The set of empirical isotherms was measured for both coal samples. Figures 2 and 3 present the sorption isotherms of CO_2 on the study samples.

Sorption levels, as expected, decrease with increasing temperature. The total capacities of carbon dioxide differ by about 40 % between coal samples, the maximum capacity for the Be sample being $25 \text{ dm}^3 \text{ STP/kg}$ and for the Tu one $35 \text{ dm}^3 \text{ STP/kg}$. However, the final sorption on both samples, calculated from the linear form of the

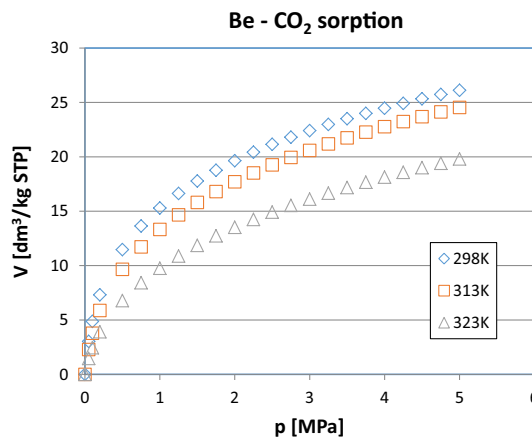


Fig. 2 Empirical sorption isotherms of CO_2 on Be sample in different temperatures

isotherm, is the same and reaches a value of 2.66 mmol/g . The calculated values of the isosteric heat of adsorption are 42.9 and 38.4 kJ/mol for the Be and Tu samples, respectively.

3 Numerical analysis

Simulations of CO_2 sorption isotherms using the MSM were carried out on the basis of the isotherms that had been measured. The model is constructed by applying the co-

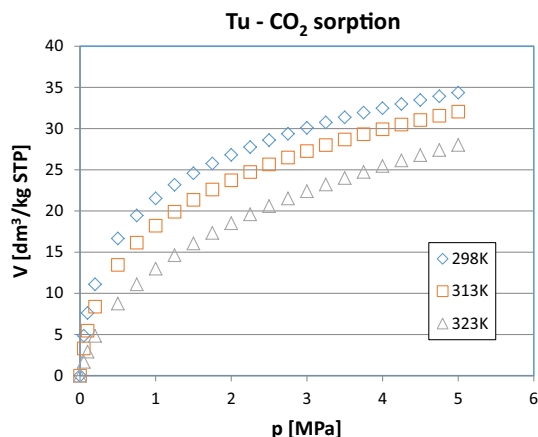


Fig. 3 Empirical sorption isotherms of CO₂ on Tu sample in different temperatures

polymeric structure of coal involving five types of objects forming the process space: (1) Arene domains—rigid, semi-crystalline structures created with condensed benzene rings; (2) Connected aliphatic, alicyclic and heterocyclic chains forming a limited rigid network together with arene domains, (3) Non-interconnected aliphatic, alicyclic and heterocyclic chains forming an elastic molecular phase which fills the inter-network spaces, (4) Pores in the coal material, (5) Mineral admixtures. The sixth component of the sorption space is the set of molecules of the sorbate, which could take any space in the network except the volume of the arene domains (Jodlowski and Wojcik 2014; Sakurovs 2012). Certainly the fraction of highly developed compounds is small in the case of lignites (Mathews et al. 2011; Mathews and Chaffee 2012). Numerous phenomena are found in the sorption process from absorption (penetration of the elastic, molecular phase of coal), expansion in pores having sizes smaller than the diameter of the sorbate molecule and adsorption on the surface in pores comparable to the adsorbate molecule size (submicropores) and in larger pores (other classes of pores). Extension is made for multilayer adsorption in bigger pores assuming the possibility of the formation of non-BET stacks due to adsorption. The model is called LBET and its properties are similar, under the boundary conditions, to the generalized Langmuir equation (for monolayer adsorption) and the already developed BET equation for poly-layer adsorption with a limitation on adsorption capacity in the layers as a result of the formation of non-BET stacks (Milewska-Duda et al. 2000).

For accurate modeling of sorption based on thermodynamic analysis, exact values are necessary of both cohesion energy and the molecule volume of gaseous sorbates. The state equation of gases for the model is developed and introduced to the computation packet (Milewska-Duda et al. 2002).

As described above in the assumption of the model simulated sorption isotherm consists of three subsystems: adsorption, absorption and expansion. In the first phenomenon adhesion forces play a major role, in the second there are only cohesive forces, while in the third placement of molecules takes place by the interaction of cohesion and adhesion forces (see Figs. 4, 5). The expansion is related to the placement of the molecules in submicropores smaller than the diameter of the sorbate molecules. In addition, it is possible to divide a priori sorption on eleven virtual subsystems from pure absorption to pure adsorption determining the distribution of volume and capacity of submicropores (see Figs. 6, 7). Molecules of penetrant (gas) are assigned to the subsystem (adsorption, absorption and expansion) based on the number of contacts, respectively to the model of the space of spheres (Duda and Milewska-Duda 1995; Jodlowski et al. 2007) and the energy of these contacts. It is assumed that the particles are generally isolated in adsorption and expansion subsystems. Their presence in these subsystems causes swelling of coal material as well as contraction of pores. While the adsorption involves formation of the space for penetrant molecule at the site previously occupied by the elements of coal material, the expansion is based on the enlarging of existing submicropores. From this point of view, adsorption requires only the action of the forces of cohesion, while in the expansion subsystem interaction of both cohesive and adhesive forces is taken into account. However, in both subsystems total energy of the molecule is calculated using the Berthelot rule as the resultant of cohesive energies of sorbate and sorbent. In the expansion subsystem the vacuum-like high energy contact is involved. A cohesive energy of sorbate is the same as in the virtual reference system in which the molecule energy is calculated by a special equation of gas state (Milewska-Duda et al. 2002). The double nature of sorption was the

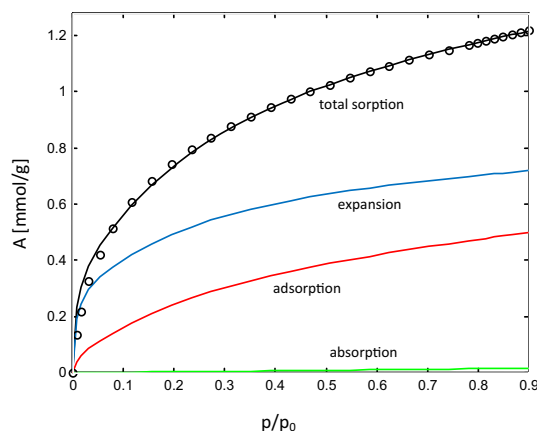


Fig. 4 Sorption isotherm of carbon dioxide on the Be coal sample in the 298 K. A adsorption given in millimoles per gram of coal matter

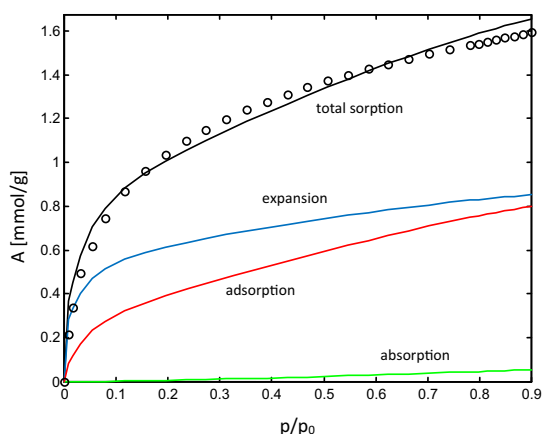


Fig. 5 Sorption isotherm of carbon dioxide on the Tu coal sample in the 298 K. A adsorption given in millimoles per gram of coal matter

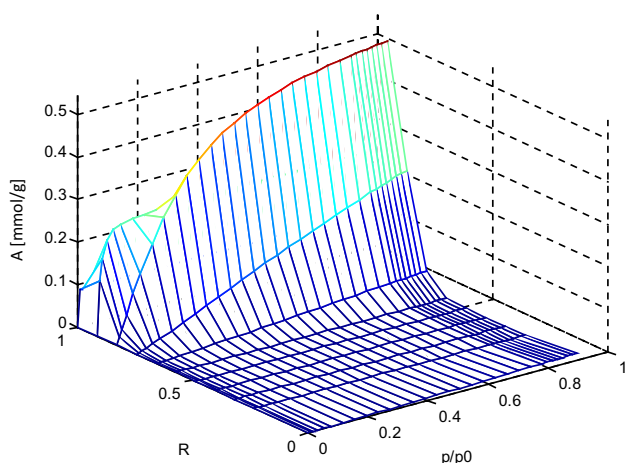


Fig. 6 Multisorption isotherms of carbon dioxide on the Be coal sample in the 298 K distribution versus relative pore radius R

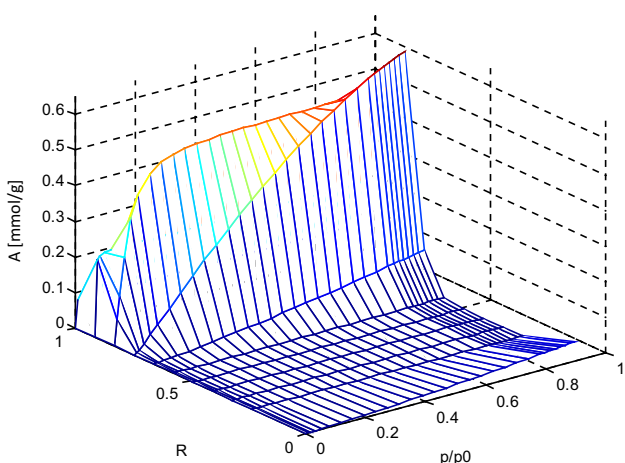


Fig. 7 Multisorption isotherms of carbon dioxide on the Tu coal sample in the 298 K distribution versus relative pore radius R

earlier approach to modelling of the phenomenon. Separation of the adsorption and expansion allows more precisely determine the effects of swelling, since the omission of the volume of submicropores (as adsorption and absorption is only assumed) overestimates the swelling.

Examples of the results of the simulation are presented in Figs. 4, 5, 6, and 7.

Scales used at the Y axes in Figs. 2 and 3 are characteristic to the conditions of the measurement using volumetric method (dm^3/kg STP). However Fig. 4 and further are produced by the program computing isotherms and sorption system properties under the MSM. Feature of the model is to use the number of moles to simulate sorption isotherms. The volume of gas is converted to the number of moles using the original equation of state incorporated into the model (Milewska-Duda et al. 2002). Therefore sorption in Figs. 4 and further is expressed in mmol/g corresponding to the amount presented in the previous figures.

Numerical results—isothersms (lines) are presented against a background of empirical data (circles) and given in millimoles per gram of coal material. Figures 4 and 5 present cumulated sorption in the subsystems. The black line represents the total theoretical sorption in the system, the red one describes adsorption, the blue one—the expansion and green demonstrates absorption. The total sorption capacity is calculated by summing the number of sorbate moles in constituent sorption subsystems. Then, the total sorption capacity in Figs. 4, 5 comprises the sum of the moles of sorbate with the subsystems adsorption, absorption, and the expansion. The first sub-system is described as comprising particles of purely adhesive interactions, the second comprises particles of cohesive interactions only, and the third is a combination of both types of interactions.

Surprisingly, the amount of absorption is small in all the isotherms computed (even in those not presented in the paper). This is an unexpected property of the lignite having a relatively large content in the molecular phase compared to sub-bituminous and bituminous coals. However, expansion is a significant process in both coal samples and at all temperatures. Such a situation is possible because of the functional groups existing in the relatively wide submicropores, greatly increasing the potential. Figures 6 and 7 present distributions of molecules in the virtual subsystems. The absorption subsystem is for a relative pore radius $R = 0$, in the range $0 < R < 1$ the expansion subsystems with different energy are described and the whole adsorption subsystem is presented for $R = 1$. The total capacity of the sorption system is calculated in the model and compared to the curve that was measured (Figs. 4, 5).

One of the parameters introduced to the model is the cohesive energy density obtained from the Hombach and van Krevelen publication (Hombach 1980; Van Krevelen

1993). Cohesion energy of coal is calculated on the basis of a detailed thermodynamic analysis of the sorption system properties and on the basis of the given cohesive energy density. Cohesion energy of sorbate (E_p) is calculated using the equation of state of gas developed specifically for the model. Subsequently, the energies of molecules in each subsystem are calculated using the Berthelot rule. For the adsorption system dimensionless parameter of adsorption energy (Q_{ads}) is calculated with the assumption that the molecule is in contact with the surface atoms with $Z < 0.5$, where Z is the ratio of the number of contacts to the maximum number of contacts in the network. For molecules of which the parameter $Z = 1$ there is absorption, the dimensionless parameter of the absorption energy (Q_{abs}) is calculated. On the basis of the energy distribution for the various sorption subsystems the average cohesion energy of sorbate in absorption-expansion subsystem is calculated (Q_p). This is the so-called cohesive energy of penetrant, which must overcome the forces of cohesion in order to locate in these subsystems.

The absorption energy Q_p is bigger than the cohesion energy of sorbates E_p (see Table 2) thus expansion is possible but penetration of coal material (absorption) is not an attractive way for the molecule to locate in the system. The values of the cohesion energy of molecules in the absorption subsystem estimated in the model are increased relative to the cohesion energy of pure sorbate. It is an effect of the application of the Berthelot rule which describes the energy of the molecule in the subsystem as the geometric mean of the cohesion energy of penetrant and coal molecules. Hence sorbate molecules in direct contact with coal molecules have a bigger cohesion energy than their energy in the liquid-like state. The energy coefficients of absorption Q_{abs} and adsorption Q_{ads} are large, suggesting the presence of high-energy sites in the adsorption subsystem and strong interactions with molecules of coal material. Lignites probably contain a large

number and diversity of functional groups, which constitute small pores. In part they are not revealed on the surface of the coal and their interactions with CO_2 molecules in the coal mass are very weak.

While analysing the multisorption isotherms in the subsystem (Figs. 6, 7), one can observe a predominant role of expansion in the system. All isotherms from the relative radius R , ranging from 0.6 to 0.9, are the effect of the location of molecules in pores of a size comparable to but smaller than the diameter of the molecule. The situation is nearly the same at all the temperatures considered.

The space in the model is represented by a virtual network of objects consisting of spherical segments constituting the 6 types of components. The ratio of the number of contacts to the maximum number of contacts (network constant) is calculated in the model. Accordingly, the ratio of contacts for small submicropores is designated ZA and, for bigger submicropores— ZB . The parameter RB defines the characteristic submicropore size for which there is a change in the nature of interaction from cohesive to adhesive. The values of geometrical parameters ZA , ZB and RB are assumed during the simulation and then changed until a satisfactory fitting of the total sorption isotherm to measurement data while maintaining reasonable thermodynamic parameters. The submicropore radius in which there is a maximum capacity (R_{av}) is calculated with model formulas adequately to the interactions of sorbate and carbon material. Values of the geometry parameters obtained in the numerical experiment are presented in Table 3.

Geometric parameters give no precise information about the influence of temperature on the behaviour changes of coal material. There are no clear trends in the ZA and ZB parameters which describe how ideal are the contacts of sorbate molecules with segments of coal material. Lower values of these parameters indicate a smaller number of contacts (worse fitting of the molecule to the surface).

Table 2 Energetic parameters of the sorption system

| Sample | T K | Q_{ads} – | Q_{abs} – | E_p kJ/mol | Q_p kJ/mol |
|--------|--------|----------------|----------------|-----------------|-----------------|
| Be | 298 | –8.07 | 11.44 | 6884.9 | 9362.6 |
| | 313 | –7.12 | 10.87 | 6885 | 9486.3 |
| | 323 | –7.02 | 9.99 | 6885 | 9497.6 |
| Tu | 298 | –10.62 | 10.58 | 6884.9 | 9362.6 |
| | 313 | –8.35 | 9.75 | 6885 | 9487.5 |
| | 323 | –7.98 | 9.17 | 6885 | 9498.3 |

Q_{ads} unit-less coefficient describing the energy of adsorption, Q_{abs} unit-less coefficient describing the energy of absorption, E_p cohesion energy of the sorbate, Q_p average cohesion energy of the sorbate in absorption-expansion system (penetrant cohesion energy)

Table 3 Geometric parameters of the sorption system

| Sample | T K | ZA – | ZB – | RB – | R_{av} – |
|--------|--------|-----------|-----------|-----------|---------------|
| Be | 298 | 0.73 | 0.82 | 0.67 | 0.92 |
| | 313 | 0.76 | 0.97 | 0.66 | 0.93 |
| | 323 | 0.75 | 0.92 | 0.66 | 0.93 |
| Tu | 298 | 0.92 | 0.82 | 0.67 | 0.88 |
| | 313 | 0.88 | 0.97 | 0.65 | 0.9 |
| | 323 | 0.89 | 0.89 | 0.64 | 0.91 |

ZA coefficient of sorbate molecule contact with coal matter for pores lower than RB , ZB coefficient of sorbate molecule contact with coal matter for pores bigger than RB , RB relative radius of pore in which cohesion energy of coal matter is equal to cohesion energy of sorbate, R_{av} relative radius of pore in which appear the maximum of submicropores distribution

From the ZA parameters one can state that smaller pores in the Tu sample fit the molecule better than the same type of pores in the Be sample. The ZB coefficient shows bigger changeability versus temperature but still not significant. It seems that an increase in temperature makes the bigger submicropores more accessible to the sorbate molecules; however, that trend is not clear and significant. The characteristic size of the pores in which the cohesion energy of coal material and sorbate is the same (RB—relative to the molecule size) is constant in the range of temperatures studied. However, the average size of pores (Rav—signifying the maximum of the submicropores distribution) changes slightly to larger values with an increase in temperature. This indicates insignificant thermal expansion of the coal material, probably together with the pores. A small difference is observed between coals in the geometric properties of the coal material. In the Be sample the fitting of the carbon dioxide molecule in both the small (Z_A) and larger (Z_B) submicropores is worse in comparison to the Tu sample, at the same time the adsorption energy (Q_{ads}) is smaller for the Be sample than for the Tu one and this has an effect in the smaller sorption capacity of the Be coal. The value of the characteristic radius of submicropores (Rav), meaning the maximum of the capacity distribution of submicropores, is slightly larger for the Be sample (see the distribution in Figs. 6, 7) but for both samples it is within the range of the expansion subsystem.

4 Conclusions

Lignites are a reasonable geological formation for carbon dioxide sequestration by means of sorption but deposits of lignites are usually located at a shallow depth, which makes them useless for this purpose. The permeability of the bed and possible leakages are another problem which needs to be investigated and solved (Gensterblum et al. 2010; Perera et al. 2011). In our study of the CO₂/lignite system, adsorption, expansion and absorption phenomena are determined. This is a known property of these lightly metamorphosed coals. Simultaneously the adsorption is of the Langmuir type and gives a very good fit to the linear form of the Langmuir equation. A set of geometric and energetic parameters of the coals and the sorption systems is estimated. The computed estimates of energetic parameters are different from the isosteric heat of adsorption calculated from adsorption data, but this was expected. This situation takes place because total sorption energy is correlated with the isosteric heat of adsorption. The MSW model takes both the cohesion and adhesion energies into account, which results in an estimation of larger values for the surface enthalpy parameters because of participation of the cohesion energy in total sorption energy (the energy

produced in the adsorption subsystem is partially consumed in the expansion and absorption subsystems).

A significant participation of expansion in total absorption may indicate a relatively strong bonding of molecules in submicropores, causing swelling of carbonaceous material. Note that the swelling results in a contraction of the pores, thereby reducing the permeability of a carbon material. This confirms reports in the literature about self-sealing deposits of lignite. The final conclusion is that with careful operations carbon dioxide sequestration in deposits of lignite would be possible.

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