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Discrepancies in the assessment of CO_2 storage capacity and methane recovery from coal with selected equations of state

Part I. Experimental isotherm calculation

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Abstract. The injection of carbon dioxide into coalbeds to increase methane recovery is an emerging technology which was tested in various pilot installations. Carbon dioxide stored in coalbeds is usually in supercritical state and therefore investigation of supercritical adsorption of this gas on coal is a subject of various studies. In the paper impact of three equations of state i.e. Peng Robinson (PR), Soave-Redlich-Kwong (SRK) and the most accurate Span-Wagner, as a reference, on the calculation of sorption capacity was investigated. Langmuir parameters were calculated on the basis of experimental results of CO_2 volumetric sorption by a Selar Cornish coal sample. It is concluded that the use of cubic equation of state (PR and SRK) for the calculation of supercritical CO_2 sorption on coal gives unreliable results by lowering apparent absolute adsorption in the lower pressure range (< 9 MPa) and unrealistically increasing it at higher pressures.

keywords: enhanced coalbed methane, carbon dioxide sequestration, equation of state, sorption by coal

1. Introduction

Enhanced Coalbed Methane Recovery is a technology that was developed in order to increase extraction of methane from coal seams and at the same time mitigate carbon dioxide emissions (Reeves 2003; Pini et al. 2007; Balan and Gumrah 2009). Pilot installations with stimulation of methane recovery by CO_2 injection have been already tested all over the World e.g. Ishikari Coal Basin in Japan (Fujioka et al. 2010), RECOPOL project in Poland (Pagnier et al. 2005), Big Fenn Valley in Canada (Mavor et al. 2004), San Juan Basin in USA (Reeves 2002). An increase of methane production from coal by ECBM technologies is obtained due to a higher affinity of CO_2 to coal resulting in displacement of methane. Once CO_2 is injected, it is permanently trapped as a dense gas in coal cleats and adsorbed on and in coal matrix.

In Europe, coalbeds saturated with methane are located below 750 meters (i.e. where pressure is above 7.5 MPa) and have temperature above 40°C. Therefore, injected CO_2 is under supercritical conditions. Not only storage capacity is an important issue but in order to consider coalbed as suitable for ECBM, the following parameters have to be assessed (Katyal et al. 2007): *P*, *T* and depth of coalbed; coalbed characteristic; type, rank, thickness of coal; mineral matter; moisture content; multi-component sorption/desorption, exchange ratio; coal matrix swelling/shrinkage during adsorption/desorption; cleat permeability and porosity.

Extensive laboratory experiments and geological survey are conducted to obtain all of the above parameters. Later, reservoir simulators are used to incorporate all the abovementioned parameters in order to give an overview of anticipated gas injection/production rates with time. One of the key parameters in ECBM is CO_2 adsorption capacity which is measured in laboratory. Such analyses are performed with the use of either manometric or gravimetric setups (Gensterblum et al. 2009; Li et al. 2010; Pini et al. 2010). On the basis of lab data sorption models such as Langmuir isotherm, BET or Dubinin-Raduschkevich are fit (Ottiger et al. 2006; Sakurovs et al. 2007; Dutta et al. 2008). Accuracy of measurements can have a significant impact on derived parameters of these models. Calculated model parameters are later key input data for reservoir simulators.

In this study, we investigate the impact of equation of state (EoS) on the Langmuir parameters calculated from the same raw laboratory data.

2. Experimental approach

2.1. Sample preparation

Table 1. Properties of U.K Selar Cornish coal used for the experiments

Proximate analysis[1]				
Moisture, wt%	Volatile matter, wt%	Fixed Carbon, wt%		Ash, wt%
0.64±0.04	9.61±0.02	85.37±0.01		4.38±0.06
Ultimate analysis[1]				
Carbon, wt%	Hydrogen, wt%	Nitrogen, wt%	Sulfur, wt%	Oxygen, wt%
85.2±1.3	3.28±0.03	0.77±0.05	0.92±0.01	5.60±0.01
Microscope analysis				
R_{max}, %	Vitrinite, vol%	Liptinite, vol%	Inertinite, vol%	Minerals, vol%
2.41	73.6	24.6	0	1.8

[1] Standard deviations reflect the variability of coal from one block used for the experiments. These values are larger for the entire coal layer

Experiments were performed on a semi-anthracite coal sample from a Selar Cornish, South Wales Coalfield. Properties of the coal are presented in Table 1. Coal used for experiments was crushed and sieved to fractions between 1.5 and 2.0 mm. Batches of 50 to 70 cm^3 were sealed and stored at temperature of approximately 276 K until the start of experiments. Before the experiment, the sample is evacuated at 322 K for 24 hours in order to remove moisture content. After evacuation the sample is weighted and placed in the cell and experiments are started.

2.2. Experimental setup and procedure

For the purpose of the study highly accurate manometric apparatus was used (Van Hemert et al. 2009). The setup consists of 5 stainless steel cells: two sample cells, two reference cells and one reservoir. Simplified scheme of the setup is presented in Fig. 1. Pressures are measured using highly accurate pressure transducers PTX611 manufactured by DRUCK (+/- 0.001% F.S). In order to keep the temperature of the experiments constant the entire setup is immersed in water bath. Temperature of the experiments is monitored using a PT100 sensor manufactured by Automated System Laboratories. The pressure and temperature sensors are connected to a data acquisition system recording data every 10 seconds.

Before starting the experiment the setup leak-proof was tested by pressurizing He at approximately 20 MPa for more than 25 hours. After the leak test, void volume of the sample cell was determined by He expansion method, with the assumption that He does not adsorb on coal.

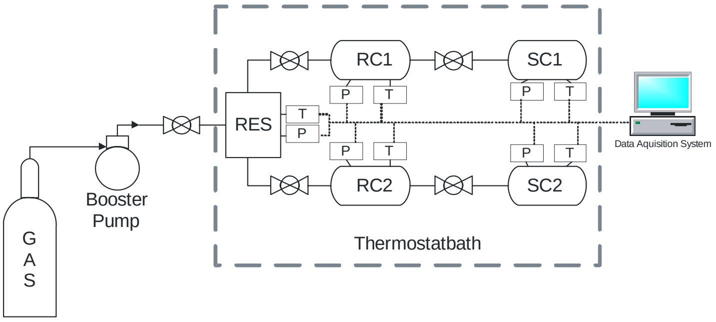

Fig. 1. Scheme of manometric sorption setup used in a study. RES is the reservoir. RC1 and RC2 are reference cells, SC1 and SC2 are sample cells, P and T are pressure transducers and thermocouples respectively

The measuring procedure consists of decompressing known volume of the gas from the reference cell (RC) to the sample cell (SC) under constant temperature. Process of physical adsorption removes adsorbate gas molecules from the free phase to adsorbed phase resulting in decrease in free gas pressure within the system. The total number of moles adsorbed during each pressure step is the difference between the total amount of gas introduced into the void volume of the sample cell and the amount of free gas occupying the void volume. Repeating this procedure in consecutive steps enables to establish an adsorption isotherm i.e. relation between gas pressure and amount of gas adsorbed under constant temperature.

Physical adsorption of gases in coal is a relatively long lasting process and in order to establish an adsorption isotherm proper equilibration times are needed. In case of carbon dioxide each pressure step may last for up to two weeks whereas for methane up to 10 days. For technical reasons equilibration time at each step was reduced to approximately 48 hours which is in agreement with other publications (Fitzgerald et al. 2005; Prusty 2008; Majewska et al. 2009).

3. Data analysis

In order to obtain adsorption isotherm it is necessary to use equation of state (EoS) for the calculation of gas density. Void volume of the sample was calculated with the use of He EoS published by McCarty (McCarty and Arp 1990). Methane sorption values were calculated using Wagner and Span EoS (Wagner and Span 1993). Carbon dioxide densities were calculated with the use of the following equations of state:

- Peng-Robinson (PR) (Peng and Robinson 1976) and Soave Redlich Kwong (SRK) (Soave 1972) – two cubic equations of state commonly used for carbon dioxide property calculation,
- Span & Wagner (SW) – recently developed accurate equation of state which accuracy up to 523 K and pressure up to 30 MPa ranges from ±0.03% to ±0.05% in the density (Span and Wagner 1996).

Figure 2 shows the carbon dioxide density at 318.15 K computed by three equations of states used in a study. It is clear that the difference in density between reference EoS (i.e. SW) and PR and SRK is much bigger in critical region i.e. above ≈ 7.3 MPa. The relative deviations of SRK and PR from the reference EoS are presented in Fig. 3. Maximum negative deviation is almost 20% in case of SRK and 10% in the pressure region of 10.0-11.0 MPa. Positive deviations are almost 3% for PR near the critical point.

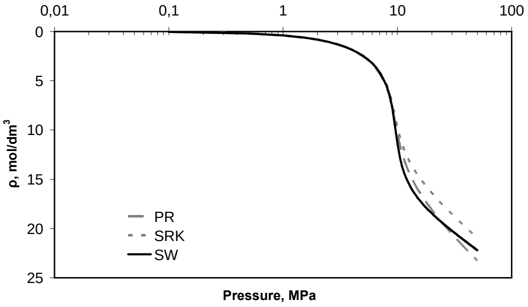

Fig. 2. Density of carbon dioxide (ρ) calculated with three equations of state used in a study (i.e. PR, SRK and SW) at 318.15 K

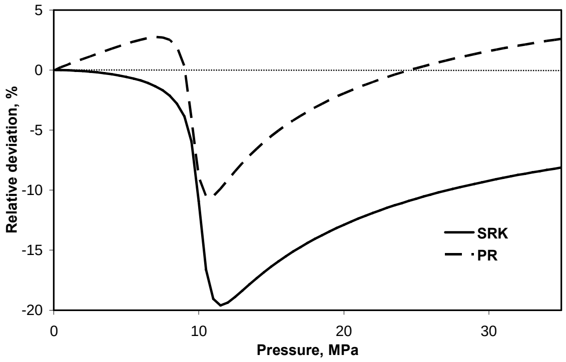

Fig. 3. Relative deviations of SRK and PR for carbon dioxide densities calculated at 318.15 K

Density of carbon dioxide ρ (in mol/m^3) is calculated as a function of P [MPa] and T [K] by EoS. The following formula was used for calculation of excess sorption m^N [mol/kg] for measurement N:

$$m^N = \frac{V_{ref}}{M}\left[\sum_{i=1}^{N}\left(\rho_{fill}^{i} - \rho_{eq}^{i}\right) - \chi\rho_{eq}^{N}\right] \tag{1}$$

where the superscript i indicates each sorption step and V_{ref} [cm^3] is the volume of the reference cell. M [g] is the mass of the coal sample after evacuation, χ is the volume ratio of the reference cell to the sample cell. Filling and equilibrium stage are denoted by subscripts *fill* and *eq*, respectively.

4. Results and discussion

4.1. Sorption isotherm and Langmuir model fitting

As indicated in the introduction, the purpose of the study was to assess the difference in the calculation of Langmuir parameters based on the isotherm computed with the use of different equations of state. Langmuir parameters are crucial input data in any coalbed methane reservoir simulator and have to be given for an absolute adsorption values in order to represent real gas adsorption of coal. Absolute adsorption can be calculated using the following formula:

$$m^A = m^N\left(\frac{\rho_{ads}}{\rho_{ads} - \rho_{free}}\right), \tag{2}$$

where m^A is the absolute amount of moles adsorbed, m^N is the excess sorption in moles, ρ_{free} and ρ_{ads} is the density of the gas in free and sorbed phase respectively. The density of carbon dioxide in adsorbed phase was calculated by extrapolating experimental data of excess sorption curve on coal to the point where it intersects horizontal axis (i.e. density of free phase reaches the density of sorbed phase) and was assumed to be 42.06 mol/dm^3. Such an approach and high values of CO_2 sorbed density were suggested also by other authors (Day et al. 2008; Pini et al. 2009;

Sakurovs et al. 2009), The density of CH_4 sorbed phase was assumed, after Sudibandriyo et al. 2003, to be equal to liquid density (26.41 mol/dm^3).

Gas sorption/desorption behaviour on coal is well described by the Langmuir model and indeed it is the most frequently model used in reservoir simulators. The most common form of the Langmuir equation for coalbed methane application is the following:

$$V = \frac{V_L \cdot P}{P_L + P} \tag{3}$$

where V is the volume of gas sorbed per unit mass of coal, V_L is a maximum gas content at infinite pressure (called Langmuir volume) and P_L is the pressure at which half of that gas is in coal (called Langmuir pressure). The Langmuir isotherm model was fitted to experimental data by minimizing the sum of squared residuals with the Excel solver.

In Fig. 4 isotherms calculated with PR, SRK and SW equations of state from the same set of experimental data are presented. It is clear that only in case of SW EoS plotted curve has a shape of type I isotherm (according to IUPAC classification) whereas use of other two equations of state gives erratic results, in particular at pressures above 5 MPa. The reason of these errors lies in the principle of manometric gas sorption measurements and deviations in density calculation by the cubic equations of state. Density of the gas in the Reference Cell calculated by SRK and PR at ~20 MPa is lower in comparison to reference SW EoS (see Fig. 3) but the density at pressures below critical point (i.e. in the Sample Cell) is calculated fairly well. Thus, established isotherm has an apparent lower adsorption at pressures up to critical point. When pressure in the Sample Cell increases above critical region errors in case of PR EoS cancel out to some extent. In case of SRK error at higher pressures is still significant and misrepresents results in the whole range. As it can be seen in Fig. 4 both PR and SRK unrealistically increase calculated sorption capacity above the critical point. The reason for it is again the error in calculated density in the pressure range of approximately 7 – 13 MPa where gas density is significantly lowered with respect to the pressure in the Reference Cell (~20 MPa). This apparently increases calculated adsorption capacity to unrealistic values. In fact, in earlier publications where cubic EoS were used this sudden increase of sorption at higher pressures was visible and could be attributed to the effect explained above (Hall et al. 1994). The above mentioned observations lead to the problem of Langmuir model fitting. Only in the case of SW EoS Langmuir isotherm fitting is satisfactory for the whole range of measured data points. However, gas adsorption on coal is commonly measured in setups which operate within the range of 0-10 MPa. Thus, it was decided to fit Langmuir isotherm model to experimental data of PR calculated points below 10 MPa where the curve has a shape of an isotherm. SRK EoS as far more inaccurate was rejected for further considerations. The calculated Langmuir parameters V_L and P_L for SW are 0.03648 sm^3/kg and 0.597 MPa respectively and for PR 0.03071 sm^3/kg and 0.406 MPa, respectively. As defined by the ECLIPSE software cubic meter of gas at standard conditions, that is at 16°C and 1013.25 hPa, per unit mass of coal under *in-situ* conditions is given as sm^3/kg.

The deviation in calculated Langmuir parameters V_L and P_L with respect to reference SW EoS is -18.8% and -31.9% respectively.

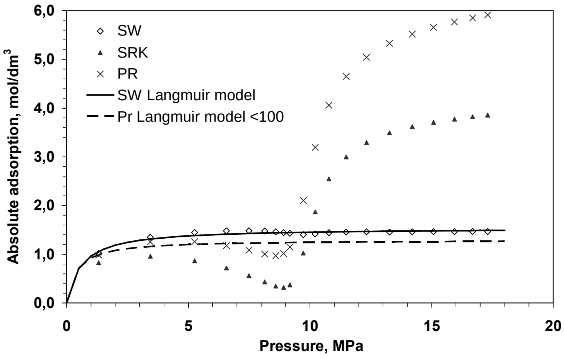

Fig. 4. Absolute adsorption calculated with three equations of state (PR, SRK and SW) and Langmuir model fitting. Note: Langmuir parameters for PR EoS were obtained by fitting experimental points up to 10 MPa

5. Conclusions

From the above study it can be concluded that the use of cubic equation of state (PR and SRK) for the calculation of supercritical CO_2 sorption on coal gives unreliable results by lowering apparent absolute adsorption in the lower pressure range (< 9 MPa) and unrealistically increasing at higher pressures. Fitting the Langmuir model into data calculated with PR is only possible for data points below ~10 MPa and lowers both Langmuir parameters (V_L and P_L). In case of data calculated with SRK EoS it is impossible to fit Langmuir model. In order to assess the impact of these deviations a sensitivity study with the use of reservoir simulator is needed and will be performed in the future.

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References

Balan H.O., Gumrah F. (2009). Enhanced coalbed methane recovery with respect to physical properties of coal and operational parameters. Journal of Canadian Petroleum Technology 48(8): 56-61.

Day S., Duffy G., Sakurovs R., Weir S. (2008). Effect of coal properties on CO_2 sorption capacity under supercritical conditions. International Journal of Greenhouse Gas Control 2(3): 342-352.

Dutta P., Harpalani S., Prusty B. (2008). Modeling of CO_2 sorption on coal. Fuel 87(10-11): 2023-2036.

Fitzgerald J.E., Pan Z., Sudibandriyo M., Robinson Jr R.L., Gasem K.A.M., Reeves S. (2005). Adsorption of methane, nitrogen, carbon dioxide and their mixtures on wet Tiffany coal. Fuel 84(18): 2351-2363.

Fujioka M., Yamaguchi S., Nako M. (2010). CO_2-ECBM field tests in the Ishikari Coal Basin of Japan. International Journal of Coal Geology.

Gensterblum Y., van Hemert P., Billemont P., Busch A., Charriere D., Li D., Krooss B.M., de Weireld G., Prinz D., Wolf K.H.A.A. (2009). European inter-laboratory comparison of high pressure CO_2 sorption isotherms. I: Activated carbon. Carbon 47(13): 2958-2969.

Hall F.E., Zhou C., Gasem K.A.M., Robinson Jr R.L., Yee D. (1994). Adsorption of pure methane, nitrogen, and carbon dioxide and their binary mixtures on wet fruitland coal. Proceedings - SPE Eastern Regional Conference and Exhibition.

Katyal S., Valix M., Thambimuthu K. (2007). Study of Parameters Affecting Enhanced Coal Bed Methane Recovery. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 29(3): 193 - 205.

Li D., Liu Q., Weniger P., Gensterblum Y., Busch A., Krooss B.M. (2010). High-pressure sorption isotherms and sorption kinetics of CH_4 and CO_2 on coals. Fuel 89(3): 569-580.

Majewska Z., Ceglarska-Stefańska G., Majewski S., Zietek J. (2009). Binary gas sorption/desorption experiments on a bituminous coal: Simultaneous measurements on sorption kinetics, volumetric strain and acoustic emission. International Journal of Coal Geology 77(1-2): 90-102.

Mavor M.J., Gunter W.D., Robinson J.R. (2004). Alberta multiwell micro-pilot testing for CBM properties, enhanced methane recovery and CO_2 storage potential. SPE Annual Technical Conference Proceedings.

McCarty R.D., Arp V.D. (1990). A new wide range equation of state for helium. Adv Cryog Eng 35, pp. 1465–1475.

Ottiger S., Pini R., Storti G., Mazzotti M. (2006). Experimental and modeling study of the adsorption of CO_2 on coal aimed at ECBM recovery. AIChE Annual Meeting, Conference Proceedings.

Pagnier H.J.M., Van Bergen F., Kreft E., Van Der Meer L.G.H., Simmelink H.J. (2005). Field experiment of ECBM-CO_2 in the upper Silesian Basin of Poland (RECOPOL). 67th European Association of Geoscientists and Engineers, EAGE Conference and Exhibition, incorporating SPE EUROPE2005 - Extended Abstracts.

Peng D.Y., Robinson D.B. (1976). A new two-constant equation of state. Industrial and Engineering Chemistry Fundamentals 15(1): 59-64.

Pini R., Ottiger S., Burlini L., Storti G., Mazzotti M. (2007). Fundamental mechanisms involved in enhanced coal bed methane recovery for CO_2 storage. Chemie-Ingenieur-Technik 79(9): 1318.

Pini R., Ottiger S., Burlini L., Storti G., Mazzotti M. (2009). Role of adsorption and swelling on the dynamics of gas injection in coal. Journal of Geophysical Research B: Solid Earth 114(4).

Pini R., Ottiger S., Burlini L., Storti G., Mazzotti M. (2010). Sorption of carbon dioxide, methane and nitrogen in dry coals at high pressure and moderate temperature. International Journal of Greenhouse Gas Control 4(1): 90-101.

Prusty B.K. (2008). Sorption of methane and CO_2 for enhanced coalbed methane recovery and carbon dioxide sequestration. Journal of Natural Gas Chemistry 17(1): 29-38.

Reeves S. (2002). Field studies of enhanced methane recovery and CO_2 sequestration in coal seams. World Oil 223(12): 56-60.

Reeves S.R. (2003). Enhanced CBM recovery, coalbed CO_2 sequestration assessed. Oil and Gas Journal 101(27): 49-53.

Sakurovs R., Day S., Weir S. (2009). Causes and consequences of errors in determining sorption capacity of coals for carbon dioxide at high pressure. International Journal of Coal Geology 77(1-2): 16-22.

Sakurovs R., Day S., Weir S., Duffy G. (2007). Application of a modified Dubinin - Radushkevich equation to adsorption of gases by coals under supercritical conditions. Energy and Fuels 21(2): 992-997.

Soave G. (1972). Equilibrium constants from a modified Redlich-Kwong equation of state. Chemical Engineering Science 27(6): 1197-1203.

Span R., Wagner W. (1996). A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. Journal of Physical and Chemical Reference Data 25(6): 1509-1596.

Sudibandriyo M., Pan Z., Fitzgerald J.E., Robinson Jr R.L., Gasem K.A.M. (2003). Adsorption of methane, nitrogen, carbon dioxide, and their binary mixtures on dry activated carbon at 318.2 K and pressures up to 13.6 MPa. Langmuir 19(13): 5323-5331.

Van Hemert P., Bruining H., Rudolph E.S.J., Wolf K.H.A.A., Maas J.G. (2009). Improved manometric setup for the accurate determination of supercritical carbon dioxide sorption. Review of Scientific Instruments 80(3).

Wagner W., Span R. (1993). Special Equations of State for Methane, Argon, and Nitrogen for the Temperature Range from 270 to 350 K at Pressures up to 30 MPa. International Journal of Thermophysics 14(4): 699-725.

Lutynski, M.A., Battistutta, E., Bruining, H., Wolf, K.A.A., Rozbieżności w ocenie ilości składowanego CO_2 i odzysku metanu z pokładu węgla jako wynik zastosowania wybranych równań stanu gazu. Część I. Wyznaczanie izotermy, Physicochem. Probl. Miner. Process., 47 (2011) 159-168, (w jęz. ang.)

Intensyfikacja wydobycia metanu z pokładu węgla za pomocą zatłaczania dwutlenku węgla jest technologią, która nie tylko przyczynia się do zwiększenia uzysku tego surowca energetycznego ale jednocześnie zmniejsza emisję CO_2. Obecnie na Świecie istnieje kilka instalacji pilotowych, w których ta technologia poddawana jest badaniom. W Europie pokłady węglowe bogate w metan występują zazwyczaj na głębokościach przekraczających 750 m i temperaturach powyżej 40°C, a więc w warunkach, w których CO_2 jest w stanie krytycznym. Adsorpcja tego gazu w stanie krytycznym na węglach jest obecnie przedmiotem intensywnych badań. Do wyznaczonych w laboratorium izoterm sorpcji dopasowywane są następnie modele sorpcyjne jak np. izoterma Langmuira, izoterma BET czy model Dubinina-Raduszkiewicza. W pracy przedstawiono wyniki badań sorpcji dwutlenku węgla na węglu antracytowym Selar Cornish z zagłębia Południowej Walii (Wielka Brytania). Do analiz wyników użyto trzech równań stanu gazu stosowanych do określenia gęstości CO_2 tj. równania Penga-Robinsowa (PR), równania Soave-Redlicha-Kwonga (SRK) oraz bardzo dokładnego równania stanu gazu dla CO_2

Spana i Wagnera (SW), jako równania referencyjnego. Do uzyskanych danych sorpcji całkowitej dopasowano model izotermy Langmuira jako powszechnie stosowany w symulatorach złożowych. Obliczone parametry izotermy Langmuira tj. VL oraz PL w przypadku równania SW wyniosły odpowiednio 0.03648 sm^3/kg oraz 0,597 MPa, natomiast dla równania PR wartości te wyniosły odpowiednio 0.03071 sm^3/kg oraz 0,406 MPa. Odchyłka w obliczonych parametrach w stosunku do równania referencyjnego dla tej samej izotermy wyniosła odpowiednio -18,8% oraz -31,9%

słowa kluczowe: intensyfikacja wydobycia metanu, sekwestracja dwutlenku węgla, równanie stanu gazu, sorpcja na węglu