GOSPODARKA SUROWCAMI MINERALNYMI

Tom 24 2008 Zeszyt 4/1

GRAŻYNA CEGLARSKA-STEFAŃSKA*, KATARZYNA ZARĘBSKA**, JANINA WOLSZCZAK**

Sorption of pure components and mixtures CO_2 and CH_4 on hard coals

Introduction

Increased amounts of CO_2 in the earth's atmosphere are believed to be the major cause of global warming. One of the methods to counteract this negative tendency involves the isolation /neutralisation of CO_2, particularly from large, concentrated industrial sources. Apart from CO_2 neutralisation in the earth's ecosystems, two alternative solutions seem practicable: trapping or sequestration of large amounts of industrial CO_2 in oceans or deep seas, or in deep strata underground (Holloway 2002). Deep underground strata are understood as hydrocarbon deposits, underground water-bearing features or very deep not mined coal seams. Several pilot projects are now underway whereby CO_2 is pumped into deep strata, for decades these techniques have been employed to intensify oil recovery. However, some problems relating to CO_2 sequestration still need to be solved. In considering sequestration, attention ought to be paid to the possible impacts CO_2 may have on the processes occurring in rocks. Obviously the rock seam must be geologically stable and the isolating layers ought to be sufficiently plastic to avoid the fissuring, so that the layers should not be interrupted. This feature is of key importance as CO_2 sequestration in these structures requires higher pressures than the hydrostatic pressure (Bachu 2002). It has to be emphasised that after the injection of CO_2 the coal seams will never be mined, as demonstrated by numerous reports in the literature on the subject of coal/ mine gas systems (Krooss i et al. 2002).

Another issue is CO_2 sequestration in abandoned coal mines and recovery of CH_4 through injection of CO_2. Different physical and chemical mechanisms are involved that in

---

* Professor, ** Ph.D., AGH-University of Science and Technology, Faculty of Fuels and Energy, Kraków, Poland; e-mail: gcegla@uci.agh.edu.pl

CO_2 injection to non-mined seams. This difference is attributable to the selective sorption of hard coals with respect to CO_2. It is well-known that the CO_2 sorption capacity is about two-times that of CH_4 of coal samples from the Upper Silesian Coal Basin in Poland. However, the results from a few recent studies indicate widely varying ratios, all the way from 10:1 for low rank coals to less than 2:1 in low and medium volatile bituminous coals (Mastalerz et al. 2004; Harpalani et al. 2006). After injecting CO_2, there will be a mixture of CO_2 and CH_4 in the seam, in the proportion depending on partial pressure of the single gases. That is why sorption processes in the coal/ gas mixture $CO_2 + CH_4$ systems have received a great deal of attention lately (Busch et al. 2003; Ceglarska-Stefańska, Zarębska 2005). This issue is also addressed in the present study. Gas mixtures used in the tests contained CO_2 and CH_4 in various proportions. The main purpose of the tests was to determine how actual proportion of CH_4 should affect the selective sorption of CO_2 from the binary gas mixture.

1. Experimental

Experiments were run on a low-rank coal from the colliery "Brzeszcze", coal specifications are summarised in Tables 1, 2, 3.

Petrographic analysis reveals the presence of large amounts of colodetrinite and scattered grains of micrinite. Telovitrinite occurs quite frequently. Intercellular spaces are small, typically filled with gehlenite or micrinite. Semifusinite is found in relative large sections of

TABLE 1

Chemical and technological analysis of the studied coal

TABELA 1

Analiza chemiczna i technologiczna badanego węgla

Elementary ingredients (% wag., daf)				VM (%)	Air-dry status	
C	H	(O+N)	S		W^a	A^a
86.00	4.50	9.20	0.30	33.40	2.88	3.90

TABLE 2

The results of the densimeter determination

TABELA 2

Wyniki pomiarów densymetrycznych

$d_{He} \cdot 10^3$ [kg · m^{-3}]	1.450
$d_{Hg} \cdot 10^3$ [kg · m^{-3}]	1.190
Total porosity [%]	17.9

TABLE 3

Maceral group analysis of studied material

TABELA 3

Analiza grup macerałów badanego materiału

Group of macerals	Maceral	[%]
Vitrinite	Telinite	15.6
	Collotelinite	3.3
	Vitrodetrinite	0.5
	Collodetrinite	27.0
Liptinite	Sporinite	12.3
	Cutinite	0.2
	Resinite	–
Inertinite	Fusinite	1.5
	Semifusinite	8.9
	Secretinite and funginite	0.5
	Macrinite	3.4
	Micrinite	7.7
	Inertodetrinit	10.4
Mineral substance		5.7
Reflectivity R_0		0.74

pressed cells or in empty voids filled with micrinite. Micrinite is a distinctive component of macerals, in the shape of grains less than 1 μm in size or stripes, or occurring in voids in tellinite or semifusinite.

An extended petrographic analysis is recommended particularly for the analysis of sorption/desorption rate in the hard coal/ mine gas systems. The currently accepted hypothesis states that glossy coals rich in vitrinite will slowly desorb gases. Another theory has it that some matt coals rich in inertinite will quickly desorb contained gases due to the predominance of large intercellular voids. The maceral content (Table 3) is a major determinant of sorption capacity, which accordingly changes with the coal rank (Karacan, Mitchell 2003; Ceglarska-Stefańska, Zarębska 2006).

Measurements were taken by the volumetric method, at the temperature 298 K and at progressing pressures. Coal samples used in the experiments were in the shape of plates 15 × 15 × 5 mm. This procedure was selected so as not to damage the natural porous structure of coal, as it is often the case when the coal samples are in the shape of grains. 20 coal plates are placed inside an ampoule. Prior to regular tests, coal samples were evacuated till the pressure 10^{-3} Pa was reached. Tested sorbates were single gases, and their mixtures with the following composition: 49.8% CH_4 + 49.6% CO_2; 73% CH_4 + 27% CO_2 and 25% CH_4 + 75% CO_2 (Linde Gas). Experiments were run in the pressure range 0–3.75 MPa. Experimental data are plotted in the form of isotherms in Fig 1. Sorption values for the tested gas mixtures are obtained in identical conditions, which renders the results fully comparable. The amounts of sorbed gas (in the mixture)is obtained from the Markham and Benton formula (Markham, Benton 1931). As soon as the maximal sorption values were obtained (≈ 4.0 MPa), the process of gas desorption would begin at gradually lowered pressure. Gas mixture from the ampoule was subject to the chromatographic analysis using a 5890 Gas Chromatograph with heat-conductive detection (Table 4). Simultaneously, the outer dimensions of coal samples were closely monitored using the strain gauges, in accordance with the procedure outlined in (Cui et al. 2004).

TABLE 4

Percentage composition by volume of the free gas desorbed from coal samples

TABELA 4

Procentowy skład objętościowy gazu wolnego, podczas desorpcji dla badanych próbek węgla

Initial composition of gas 73% CH_4 + 27% CO_2

p_{des} [MPa]	CH_4 [%]	CO_2 [%]
$p_1 = 2.47$	74.1	14.2
$p_2 = 1.76$	73.3	15.6
$p_3 = 1.26$	68.1	11.2
$p_4 = 0.84$	67.1	9.1

Initial composition of gas: 25% CH_4 + 75% CO_2

p_{des} [MPa]	CH_4 [%]	CO_2 [%]
$p_1 = 2.13$	36.5	62.8
$p_2 = 1.24$	40.0	58.3
$p_3 = 0.96$	41.8	57.5
$p_4 = 0.73$	39.6	59.7

2. Results and discussion

Tests reveal that dimensions of sorbate molecules and the pore structure are major factors affecting the selective gas sorption and diffusion. Typically diffusion in coal micropores is activated whilst diffusion capability markedly decreases with an increase of the kinetic molecule diameter (the differences of the order of *a* [cm^3NTP/g] for single gases CO_2 and CH_4). Diffusion capability of CO_2 is normally larger that that of CH_4 as their kinetic diameters are expressed by the relationship: CO_2 (0.33 nm) < CH_4 (0.38 nm).

Because of their small dimensions, linear shape and higher sorption energy, carbon dioxide molecules easily penetrates limited spaces and hence can be selectively sorbed in the internal surfaces of micro- and submicropores (~ 0.6 nm). On account of different critical temperatures of the two gases and hence physical and chemical properties at the temperature of the experiment as well as electrical properties of CO_2 (a quadruple moment)and chemical structure (oxygen groups)as well porous structure of tested coals (Table 1–3), carbon dioxide displays better sorption affinity than CH_4 in pores with various dimensions. In addition to it relatively smaller kinetic diameter, adsorption energy of CO_2 is also larger than that of CH_4 for most pore size. Therefore, carbon dioxide can diffuse into the microporous coal matrix more easily than methane. It is known that coal has a heterogeneous, interconnected pore network. If this network is constricted by ultramicropores with pore width less than 0.6 nm, it may allow CO_2 (0.289 nm halfwidth) to penetrate, while being prohibitive for CH_4 (0.310 nm halfwidth). Sorption and expansion isotherms (Fig. 2) indicate that diffusion capacity of gases tends to decrease with an increase in gas pressure, which might be attributable to the swelling of the coal matrix free gas. Similar observations are suggested by Cui et al. (Cui et al. 2004).

It is readily apparent (see Fig. 1) that the sorption capacity of coal with respect to the tested gas mixture tends to be larger for CH_4 and lower for CO_2, no matter what the actual

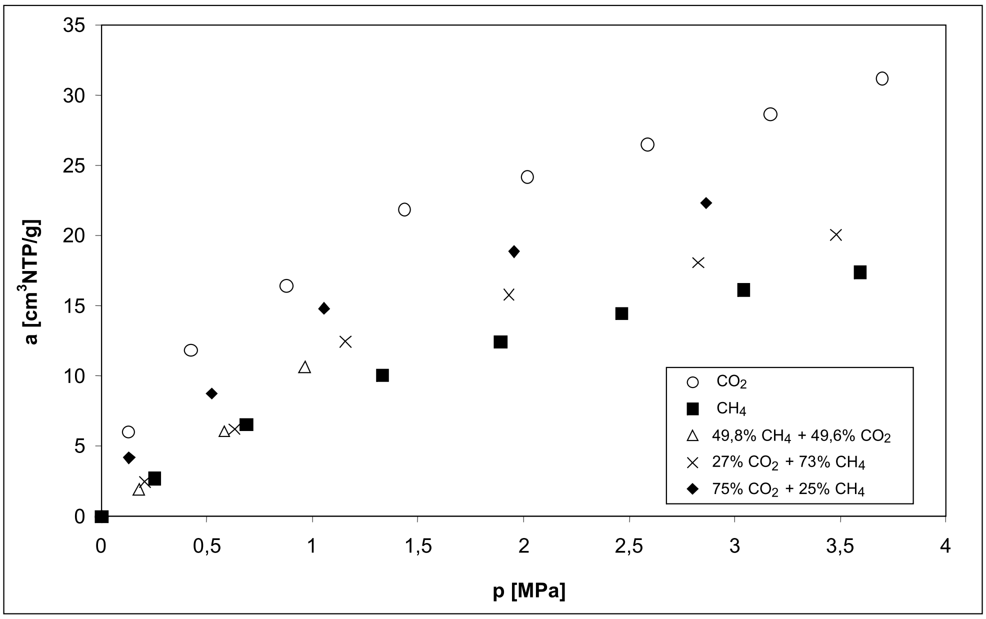

Fig. 1. Sorption of gases on studied coal

Rys. 1. Sorpcja gazów na badanym węglu

proportion of gas mixture components. Throughout the investigated pressure range the sorption capacity of coal tends to decrease with the increase in methane contents in the initial mixture. At the temperature of the experiment methane molecules have much larger kinetic energy than carbon dioxide (below the critical temperature), hence it is reasonable to suppose that CH_4 molecules will block the fissure-like and conical pores, preventing an easy access of CO_2 to the pore network. This dependency is more marked at pressures below 0.65 MPa. In this pressure range of methane and gas mixtures: 73% CH_4 + 27% CO_2 and 49.8% CH_4 + + 49.6% CO_2 sorption capacity of the tested coal is nearly the same. It has to be emphasised that maceral content (particularly inertinite groups)is a major determinant of the sorption process (Table 3). Porosity tests reveal that microstructures rich in inertinite have higher porosity that those rich in vitrinite and liptinite. That fact might be attributable to the presence

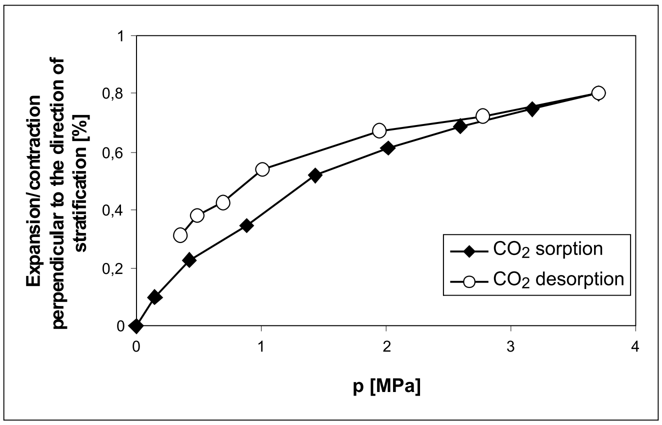

Fig. 2. Expansion/contraction (perpendicular to the direction of stratification) isotherm of CO_2 on studied coal

Rys. 2. Izotermy rozszerzania/kontrakcji (prostopadle do warstwowania) badanego węgla pod wpływem CO_2

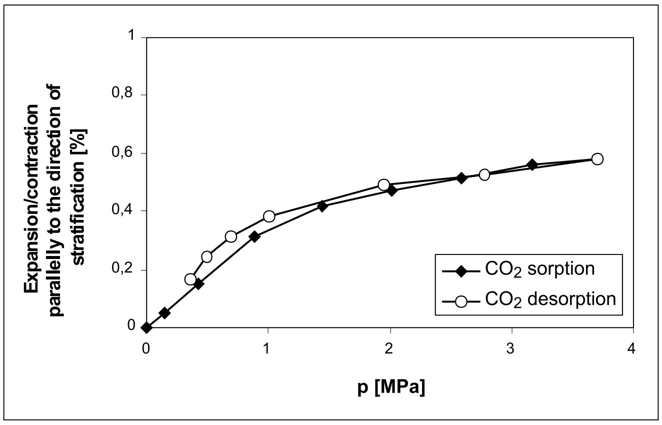

Fig. 3. Expansion/contraction (parallelly to the direction of stratification) isotherm of CO_2 on studied coal

Rys. 3. Izotermy rozszerzania/kontrakcji (równolegle do warstwowania) badanego węgla pod wpływem CO_2

of mezo- and macro- pores in intertinite, whilst the vitrinite and liptite structures are mostly microporous (Ceglarska-Stefańska, Zarębska 2002). This hypothesis is supported by densitometric data – high porosity (Table 2) and sample contraction accompanying desorption, shown in Fig. 2, 3. The absence of hysteresis for the early stages of CO_2 desorption and sample contraction in the direction parallel to the bedding plane suggest that the largest portion of gases is accumulated as free gas in the coal structure or trapped in the coal matrix due to swelling, when coal is penetrated by CO_2 molecules.

Chromatographic analyses (Table 4) for two gas mixtures with the inverse proportions of gases reveal an evident correlation between the proportion of gases in the mixture and the composition of the desorbed gas when passing from $p_1$des to $p_4$des. The proportion (in percentage) of methane to carbon dioxide in desorbed gas is ten-fold higher for an initial mixture rich in CH_4 in relation to that containing 25% CH_4 and 75% CO_2. It appears that injection of low concentration CO_2 to the seams will enrich the desorbed mixture in methane. Carbon dioxide molecules are smaller, linear in shape and have a higher sorption energy, which limits their mobility, easily penetrate into limited spaces and can be selectively sorbed in the inner surfaces of micro- and macro-pores bringing about the desorption of previously absorbed/adsorbed methane.

Conclusions

Strong dependence of the sorption process on the gas identity might have serious consequence in the context of gas recovery and CO_2 injection to coal seams for the purpose of sequestration.

Coal swelling accompanying sorption and contraction during desorption might strongly impact on the gas transport phenomena in coal seams.

Porous structure of the material affects the kinetics of gas transport, hence in modelling sequestration the CO_2 affinity to the rock surface has to be accounted.

Financial support for this study was provided by AGH framework No. 11.11.210.117

REFERENCES

Holloway S., 2002 – Underground sequestration of carbon dioxide – a viable greenhouse gas migration option. Proceedings of the 5th Int. Symp. On CO_2 Fixation and the Efficient Utilization of Energy. March 4–6. Tokyo Institute of Technology, Japan, 373.

Bachu S., 2002 – Sequestration of CO_2 in geological media in response to change climate: road map of site selection using the transform of geological space into the CO_2 phase space. Energy Conversion and Management, 43, s. 87–102.

Krooss B.M., van Bergen F., Gensterblum Y., Siemons N., Pagnier H.I.M., David P., 2002 – High-pressure methane and carbon dioxide adsorption on dry and moisture – equilibrated Pennsylvanian coals. Int. Journal of Coal Geology, 51, s. 69–92.

Mastalerz M., Gluskoter H., Rupp J., 2004 – Carbon dioxide and methane sorption in high volatile bituminous coals for Indiana, USA. Int. Journal of Coal Geology, 60, s. 43–55.

Harpalani S., Prusty B., Dutta P., 2006 – Methane/CO_2 sorption modeling for coalbed methane Production and CO_2 sequestration, Energy and Fuels, 20, s. 1591–1599.

Busch A., Gensterblum Y., Krooss B.M., 2003 – Methane and CO_2 sorption and desorption measurements on dry Argonne premium coals: pure components and mixtures. Int. J. Coal Geol., 55, s. 205–224.

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

Karacan Ő.C., Mitchell G.D., 2003 – Behavior and effect of different coal microlithotypes during gas transport for carbon dioxide sequestration into coal seams. Int. J. Coal Geol., 53, s. 201–217.

Ceglarska-Stefańska G., Zarębska K., 2006 – Carbon dioxide and methane sorption in high volatile coals from KWK Brzeszcze. Karbo,1, s. 31–34.

Markham E.C., Benton A.F., 1931 – J. Am. Chem. Soc., 53, s. 497–506.

Ceglarska-Stefańska G., Zarębska K., 2002 – Expansion and contraction of the variable rank coals during the exchange sorption of CO_2 and CH_4. Adsorption Science & Technology, vol. 20, No. 1, s. 49–62.

Cui X., Bustin R.M., Dipple G., 2004 – Selective transport of CO_2, CH_4, and N_2 in coals: insights from modeling of experimental gas adsorption data, Fuel, 83, s. 293–303.

SORPCJA POJEDYNCZYCH GAZÓW CO_2 I CH_4 ORAZ ICH MIESZANINY NA WĘGLACH KAMIENNYCH

Słowa kluczowe

Węgiel kamienny, sorpcja CO_2, CH_4, sorpcja mieszaniny, sekwestracja

Streszczenie

W pracy przedstawiono wyniki badań laboratoryjnych ukazujących znaczenie wielu czynników związanych z sekwestracją CO_2 w pokładach węgla. Są to istotne informacje, umożliwiające uzyskanie danych dotyczących interakcji CO_2 z węglem i prognozowanie ewentualnych skutków długoterminowego izolowania CO_2. Podziemne magazynowanie CO_2, umożliwia ograniczenie jego emisji, oczekując na rozwój alternatywnych źródeł energii. CO_2 może być magazynowany w głębokich i przepuszczalnych pokładach, odizolowanych poprzez przykrywające, nieprzepuszczalne warstwy skalne. W celu prognozowania długookresowego magazynowania oraz biorąc pod uwagę długookresową stabilność takiego układu, niezbędne jest dokładne poznanie fizycznych właściwości węgli. W tym celu należy dokładnie przeanalizować izotermy sorpcji, które dostarczają pożądanych w tym celu informacji. Eksperymenty zostały przeprowadzone na niskouwęglonym węglu (VM 33.4%), wyciętym z bryły macierzystej w formie płytek o wymiarach 15 × 15 × 5 mm. Pomiary przeprowadzono standardową metodą objętościową w temperaturze 298K. Zastosowane sorbaty to pojedyncze gazy: CO_2 i CH_4 oraz ich mieszanina w zmiennych proporcjach. Badania wykonano w zakresie ciśnień od 0–4 MPa. Dane sorpcyjne oraz analiza chromatograficzna desorbowanego gazu przedstawiają istotną zależność między faktycznym składem mieszaniny w ampułce a kompozycją odbieranego gazu. Niska zawartość ditlenku węgla w wyjściowej mieszaninie świadczy o wzbogaceniu desorbowanego gazu w CH_4, co potwierdza uprzywilejowaną sorpcję CO_2. Czynnikiem kontrolującym selektywną sorpcję gazów jest mikroporowata struktura oraz typ węgla, odznaczający się różną porowatością oraz rozszerzalnością, spowodowaną obecnością gazów w strukturze porowatej. Zaobserwowano silne i określone interakcje między sorbatem a porami, jak również naprężenia wywołane rozszerzalnością matrycy węgla, których wpływ na procesy transportu gazu musi być brany pod uwagę podczas modelowania składowania gazu i procesów odzyskiwania metanu.

SORPTION OF PURE COMPONENTS AND MIXTURES CO_2 AND CH_4 ON HARD COALS

Key words

Hard coal, sorption of CO_2 ,CH_4, sorption of mixture, sequestration

Abstract

The paper compiles the results of laboratory tests conducted to highlight the various aspects related to CO_2 sequestration in coal seams. It is therefore worthwhile to gather the information available on the interactions of CO_2 with coals and the effects of CO_2 on coals' properties in order to attempt a prediction of the long-term effects of sequestration. Underground storage of CO_2 allows for emission reduction, awaiting the development of other sources of energy. CO_2 can be stored in deep and permeable rocks isolated by overlying impermeable rock strata. In order to predict the CO_2 storage capacity of a candidate coal seam and to model its long-term stability, physical properties of the coals must be known accurately. Thus, the sorption isotherms of CO_2 on coal need to be treated carefully in order to obtain the desired information. The experiments were run on a low-rank coal samples (VM 33.4%)in the form of plates 15 × 15 × 5 mm. The experiments were conducted following the standard volumetric method at the temperature 298K, using the volumetric method. Tested sorbates were pure gases: CO_2 and CH_4 and their mixtures in variable proportions. The considered pressure range was 0–4 MPa. Sorption data and chromatographic analyses of gas mixture released during desorption reveal a clear dependence between the actual proportions of the mixture in the ampoule and the composition of desorbed gas. Low concentration of CO_2 in the initial mixture causes the desorbed gas mixture to be enriched in CH_4, evidencing a preferential sorption of CO_2. The factor controlling the selective sorption of gases is the microstructure of coal types in the sample, as they display various porosity and swelling rate due to the presence of gases in the porous structure. Strong and specific interactions were observed between the sorbate and pores as well as stresses due to the swelling of the coal matrix, so their influence on the gas transport processes must be accounted for whilst modelling the gas storage and methane recovery operations.