

Application of multiple sorption model to estimation of CO₂ sequestration capacity or CH₄ recovery in polish hard coals

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Abstract. The aim of the study is to estimate the theoretical capacity of coal deposits in terms of carbon dioxide storage and methane recovery estimate during the injection of carbon dioxide. The Multiple Sorption Model was used for this purpose. The range of sorption measurement data on which the simulations were based does not exceed the critical point for both methane and carbon dioxide. The model allows to calculate absorption, adsorption, expansion and total theoretical sorption. For further consideration absorption was used as the process of the percolation of the gas in the bulk of the coal matter as well as the total theoretical sorption, the occurrence of which is possible due to the presence of fractures in the coal seam. Calculated levels of absorption and the total theoretical adsorption were applied to estimate the possible storage capacity of carbon dioxide based on the data associated with the content of coal in the mining fields of individual Polish coal mines. Moreover, MSM development for the gas mixture sorption can be used to roughly assess the recovery of methane naturally occurring in coal deposits during such a process.

1 Introduction

Mitigation of carbon dioxide pollution is the focus of various works and investigations. The most popular method is the storage of gas in the geological structures [1]. These geological methods are partially used, such as pumping in of CO₂ to exhausted oil deposits – Enhanced Oil Recovery or injection of this gas into a coal deposit with simultaneous CH₄ recovery [2-6]. An interesting alternative to carbon dioxide sequestration is the storage of this gas in the coal bed of a closed colliery or in unmineable coal seams. The latter option is appropriate to deep coal deposits whose exploration is not reasonable from the economic point of view and the depth causes the necessity of CO₂ compression up to overcritical liquid but the first option does not require such high conditions. Introduction of CO₂ to a coal bed eventually gives the possibility of to recover CH₄ and to use it as a fuel. Enhanced Coal Bed Methane (ECBM) is a commonly used approach to analyse the process of methane recovery [3,7-11].

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The proposed alternative view to a rough analysis of this process on the basis of *ex situ* measurements is the application of Multiple Sorption Model (MSM). The model involves a theoretical description of the molecule of gas location in the bulk or on the surface of coal substance developed on the basis of detailed thermodynamic considerations.

2 Multiple Sorption Model

The MSM model is based on the copolymer representation of coal substance. The main components of the coal substance are:

- arene domains – semi-crystalline, rigid forms composed of plates of condensed benzene rings, building aggregates of several flakes;
- crosslinked chains – semi-rigid forms of aliphatic, alicyclic and heterocyclic chains connected with each other and with arene domains;
- non-crosslinked chains – the elastic part of coal substance consist of aliphatic, alicyclic and heterocyclic free chains;
- pores – empty spaces in coal substance;
- mineral admixtures – small aggregates dispersed in coal material whose influence on the sorption process is negligible. [12]

Arene domains and crosslinked chains constitute a limitedly rigid macromolecular phase which simultaneously constitutes the network and enables non-crosslinked chains to flow (crawl) between cells of the network. The participation and structure of the above-mentioned components of carbon structure are the input parameters of the model. Their values were obtained by pre-evaluation of the dual sorption model in the way of optimization of structure parameters with respect to the experimental data. Another set of independent parameters describes the texture of the coal adsorbent and distribution of sorbate molecules to different sorption subsystems.

Generally speaking, the coal substance is presented in the MSM model by the network of cells which have the size of methylene segments of the chain. Every object is constructed by the segments with the rule of the prohibition of occupation of the cell by multiple segments of the different objects. The exception to this rule is for pores and sorbate molecule segments.

The starting point of considerations for the model is the formula of free energy:

$$\Delta F = \Delta H + T\Delta S \quad (1)$$

which lead to the complex formulas describing: (i) absorption of molecules in the elastic part of coal material with the simultaneous creation of the space for a molecule (this space is occupied by the coal substance segments before molecule location); (ii) expansion – location of sorbate molecule in submicropores whose size is smaller than molecule size and whose dimensions should be increased; (iii) adsorption on the surface of pores whose size is greater than molecule size. Absorption and expansion is accompanied by contraction of pores (decreasing of dimensions of existing pores). Expansion and contraction results in the coal mass swelling, which is taken into account in the model calculations and is a measurable parameter. Literally speaking, the sorption system is divided into eleven subsystems containing absorption (relative pore radius $R=0$), nine expansion subsystems, giving the distribution of molecules in submicropores ($0 < R < 1$) and adsorption ($R > 1$).

Creation of pore or its expansion is done by the forces of cohesion of coal material, and location on the surface occurs due to adhesion forces. In molecular scale the surface is presented by the set of spheres and their contacts. The number of contacts, character (cohesive/adhesive) and value of its energy determines the molecule direction to the subsystem. Therefore the molecule in the absorption subsystem has number of contacts $Z=12$ (the constant of the network) and a completely cohesive character, in the adsorption system

1<Z<6 and completely adhesive character, in the sub-processes between above (expansion subsystems) 1<Z<12 and mixed character of interactions.

In conclusion, MSM makes it possible to determine the number of moles of sorbate present in each of the subsystems (distribution sorption capacity) and parameters of porous structure of a coal. The analysis of the results and the development of a model for the sorption of gas mixtures may determine the effects of competitive sorption.

3 Results of sorption modeling

In order to evaluate the numerical experiment involving the simulation of sorption isotherms, a set of isotherms of CO₂ and CH₄ measured in the laboratory is used. A sorption isotherm of a mixture of CH₄ + CO₂ has also been used for the numerical analysis. Parameters of coals used in this study are presented in Table 1.

Table 1. Parameters of coal samples used for the model

Sample	d _{He} [g/cm ³]	d _{Hg} [g/cm ³]	Ultimate analysis			Proximate analysis			
			A ^a	W ^a	V ^{daf}	C ^{daf}	H ^{daf}	S ^{daf}	(O+N) ^{daf}
31	1.387	1.230	15.50	1.65	40.90	79.60	5.00	0.71	14.69
32	1.36	1.255	2.48	3.76	40.80 ^(a)	80.88	5.26	0.62 ^(a)	13.14
34	1.35	1.23	6.15	1.55	29.20	86.40	4.9	0.8	8.37
35	1.36	1.306	16.64	1.32	32.68 ^(a)	86.55	5.22	0.90 ^(a)	7.37
37	1.4	1.30	7.78	1.25	27.90	87.60	4.88	n.a.	6.41
41	1.29	1.26	2.27	b.d.	22.43	90.08	4.76	n.a.	4.13
42	1.43	1.357	3.70	0.81	6.09 ^(a)	92.41	3.02	0.46 ^(a)	4.09

d_{He}, d_{Hg} – mercury and helium density, respectively;

contents: A – ash, W – moisture, V – volatile matter; C – Carbon, H – Hydrogen, S – Sulphur, O – Oxygen, N – Nitrogen;

indexes: a – analytical state, daf – dry and ash free

Sorption isotherms of CO₂ and CH₄ measured up to 3.4 MPa were used for evaluation of the computed set of isotherms. The MSM model was described in previous articles [12-14]. The results that were obtained are presented on Figures and Tables 2 and 3.

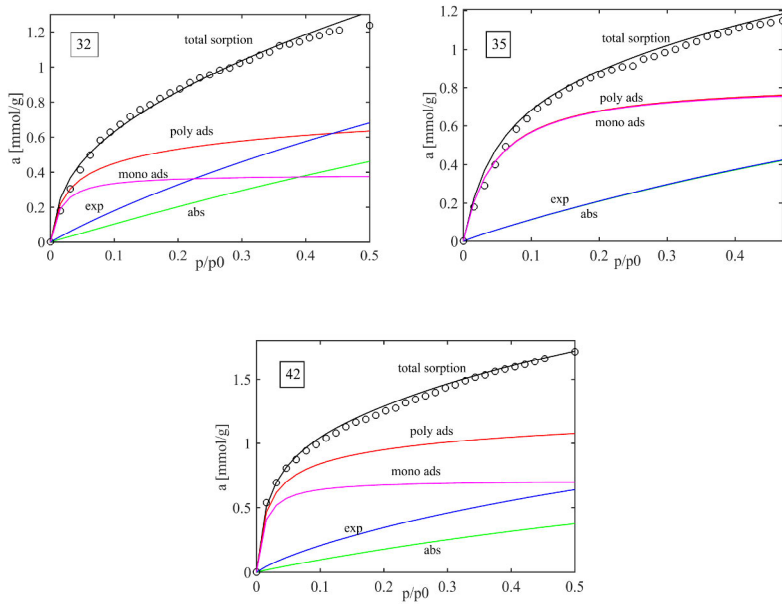


Fig. 1. Multi-sorption isotherms of **carbon dioxide** in selected samples of coal (number of samples: 32, 35, 42). Description of curves: black – theoretic total sorption, red – polylayer adsorption (poly ads), purple – monolayer adsorption (mono ads), blue – expansion (exp), green – absorption (abs), circles – experimental sorption.

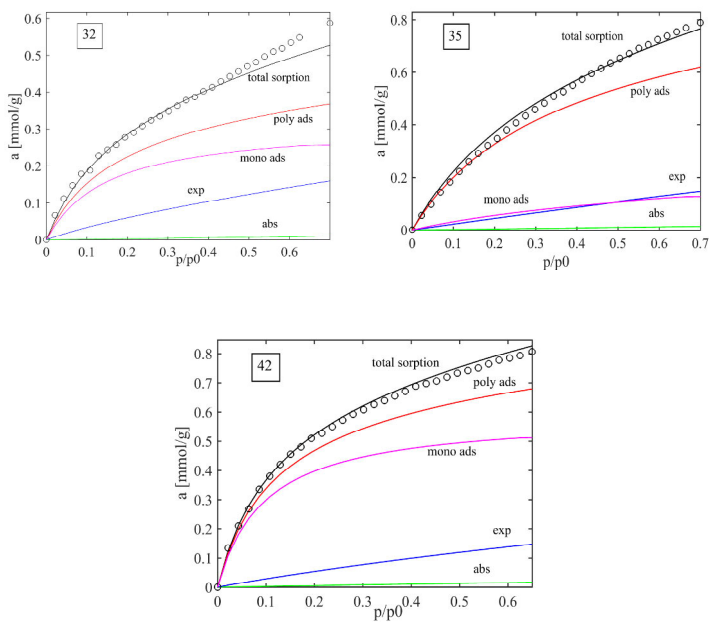


Fig. 2. Multi-sorption isotherms of **methane** on selected samples of coal (number of samples: 32, 35, 42). Curves description is the same as in Fig. 1.

One could observe a relatively big participation of absorption and expansion in the total sorption phenomenon in Fig. 1. In the case of sample 35 the sorption process has a completely dual character – expansion is negligible. Only this sample shows such behaviour and it will be presented in Fig. 3.

Methane interacts with coal substance in a different way than carbon dioxide, and this is represented in Fig. 2 by negligible absorption. Even the expansion sub-process has smaller participation in the sorption process. Thus, methane is located mainly on the surface of pores and adsorption is taking a greater share of sorption with an increasing coal rank.

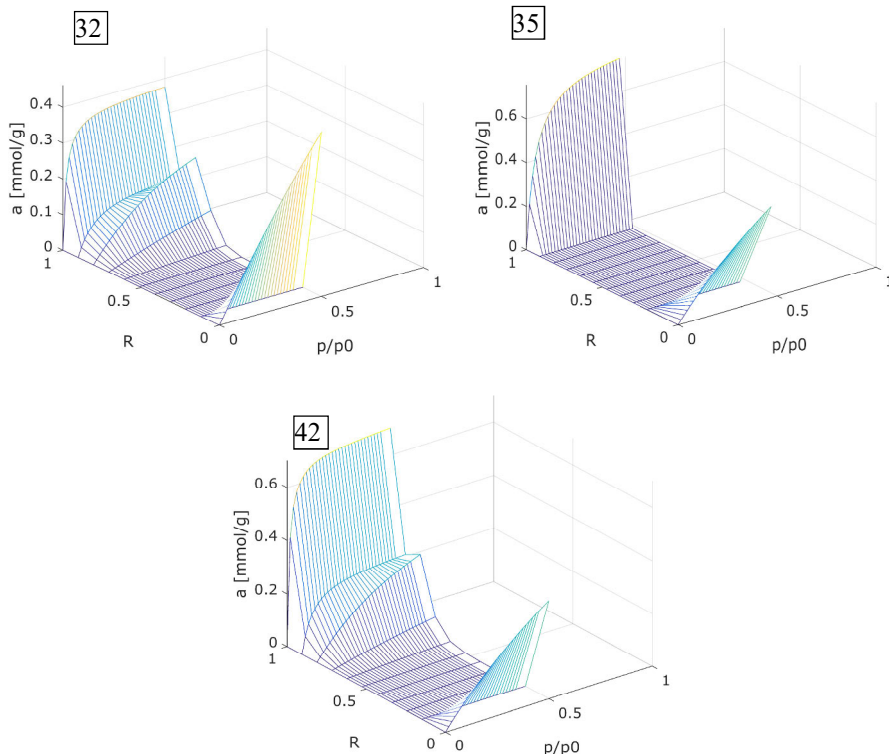


Fig. 3. Poly-sorption of **carbon dioxide** on selected samples of coal (number of samples: 32, 35, 42). Markings on the chart: a – sorption in mmol/g, R – radius of pore relative to molecule size, p/p_0 – relative pressure.

Figure 3 shows the set of theoretical isotherms representing the different size of pores (sub-micropores) forming the distribution of molecules to the sub-systems connected with pore radius (R) relative to molecule size. Sample 35 shows dual character (what was stated below in Fig. 1). In this case every expansion sub-system is empty and two isotherms of adsorption and absorption summarise the total sorption capacity of this sample. The remaining samples do not exhibit similar behaviour.

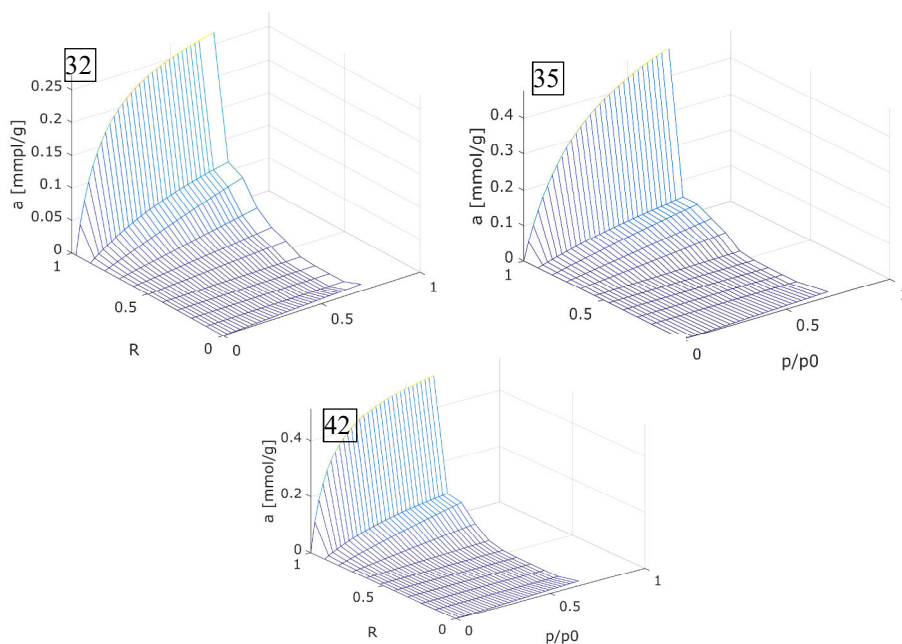


Fig. 4. Poly-sorption of **methane** on selected samples of coal (number of samples: 32, 35, 42). Markings on the chart: a – sorption in mmol/g, R – radius of pore relative to molecule size, p/p_0 – relative pressure.

Isotherms of methane poly-sorption show negligible absorption (the same as in the case of multisorption presented in Fig. 2) and the small amount of sorbate molecules in expansion sub-systems. Thus the distribution of molecules capacity is relatively flat in comparison to carbon dioxide capacity distribution (Fig. 3).

Table 2. Calculated sorption capacities in subsystems using MSM for CO₂ at $p=3.4$ MPa

CO ₂ capacity		Sample						
		31	32	34	35	37	41	42
Total sorption	mmol/g	0.747	0.763	0.930	1.180	0.875	0.830	0.800
Adsorption		0.483	0.608	0.740	0.901	0.765	0.675	0.638
Expansion		0.205	0.270	0.186	0.280	0.145	0.150	0.163
Absorption		0.090	0.148	0.178	0.133	0.140	0.148	0.163

Total sorption capacity initially increases with coal rank to achieve the maximum in the range of coals ortho-coking, then it begins to decrease slightly. It is worth noting that the absorption takes a significant part in the whole process of sorption similarly to expansion. Both sub-processes take place with the overcoming of the cohesive forces of the carbonaceous material and takes place in the bulk phase of coal deposit. Expansion and absorption give the volume tension on the coal mass what results in contraction of free pores. Eventually all these three phenomena cause the swelling of coal. Normally, in coal bed conditions, swelling is limited by the surrounding rocks and thermodynamic equilibrium shifts in favor of dissolution phenomena (absorption and expansion) in coal mass. Simultaneously, swelling results in self-sealing of the deposit after injection of CO₂ [5].

Table 3. Calculated sorption capacities in subsystems using MSM for CH₄ at 3.4 MPa

CH ₄ capacity		Sample						
		31*	32	34*	35	37	41	42
Total sorption	mmol/g	0.384	0.523	0.326	0.765	n/a	n/a	0.827
Adsorption		0.2922	0.3656	0.2257	0.6127	n/a	n/a	0.6542
Expansion		0.075	0.148	0.099	0.1385	n/a	n/a	0.157
Absorption		0.0168	0.0094	0.0013	0.0138	n/a	n/a	0.0157

* - isotherms and computations for pressure range up to 1.8 MPa

Total sorption of methane is smaller than for carbon dioxide (see Table 3), except of anthracite. Probably it is an effect of decreasing of the participation of elastic (molecular) phase in the coal substance. This fact alone shows the differences in the interaction of methane and carbon dioxide molecule to the carbon substance. Carbon dioxide penetrates the bulk phase of coal, and methane is located on the surface of the pores, resulting in negligible absorption of methane. The shape of the methane molecule results in increased tendency to form aggregates on the surface, as opposed to carbon dioxide. In this way, also the adsorption of methane is lower than the carbon dioxide because the aggregates of methane molecules may block access to sub-micropores.

An attempt was made to develop a model for the calculation of adsorption from gas mixtures. The results of the calculations are presented in Figure 5.

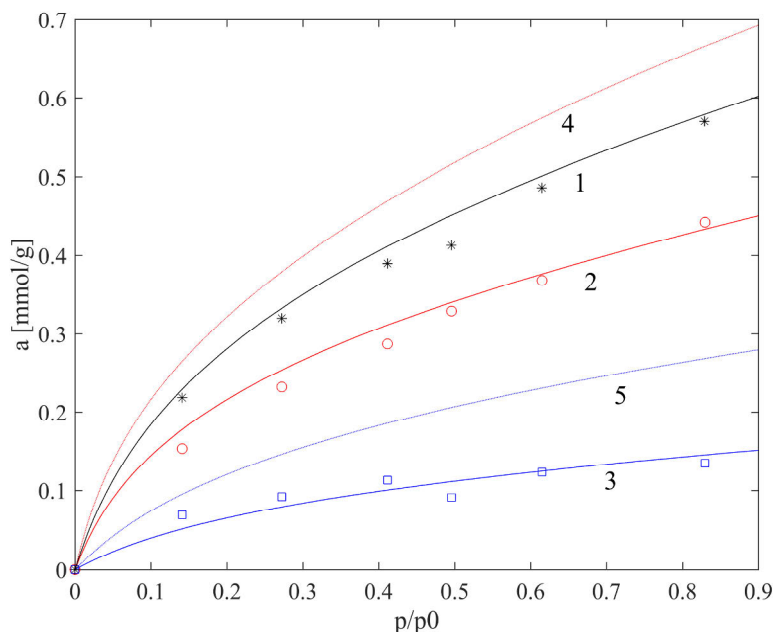


Fig. 5. Multisorption isotherm of methane and carbon dioxide mixture on a 34 coal sample. Chart description: experimental data on sorption from gas mixture – circles (CH₄), squares (CO₂) and asterisks (mix), 1 – theoretical total sorption from the mixture, 2 – theoretic total sorption of CH₄ from mixture, 3 – theoretic total sorption of CO₂ from mixture, 4 – individual sorption of CH₄, 5 – individual isotherm of CO₂.

Sorption isotherms of methane and carbon dioxide are computed on the basis of individual sorption isotherms of these gases. The analytic formula of energy of mixing process for the mixture of gases is used for derivation of isotherms of the sorption of these gases from their mixture. However, for methane this decrease is greater in all the analyzed cases. We managed to get a satisfactory but not perfect consistency model simulations with measurements carried out in the laboratory (see fig. 5). The same procedure was carried out to the remaining sorption systems presented in this work, except samples 31 and 41 because of the lack of experimental data of methane sorption in these samples.

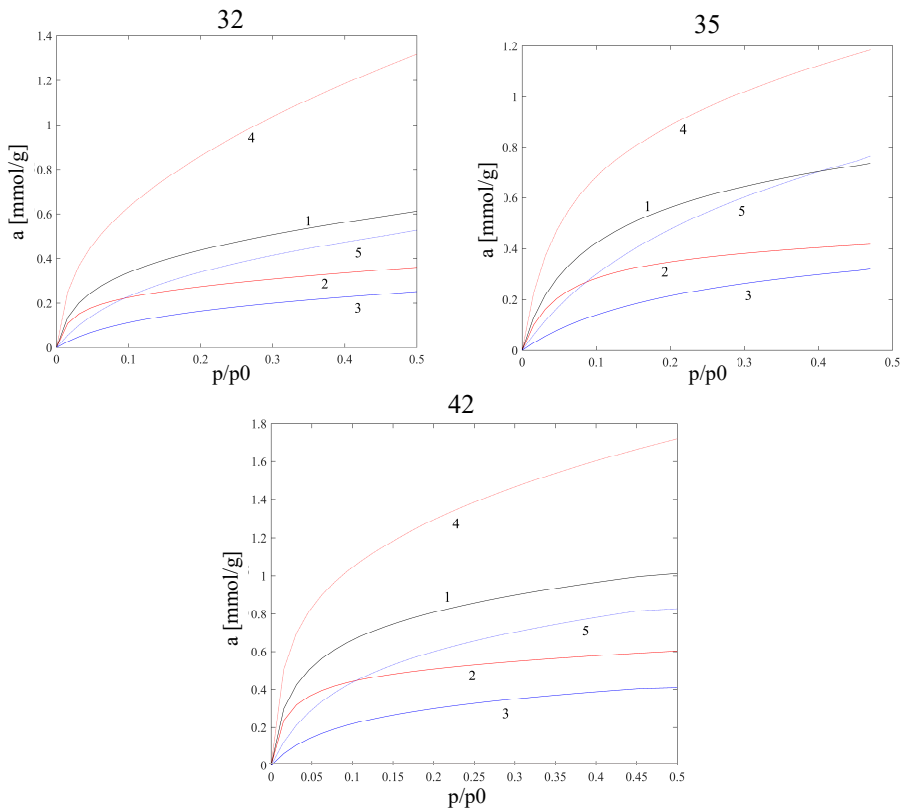


Fig. 6. Multisorption isotherm simulations of sorption from CO₂ and CH₄ mixture (number of samples: 32, 35, 42)

The decrease of methane capacity in the sorption system for the mixture of gases in comparison to sorption of an individual gas was significant in every case and it oscillated between 30 and 50%. This fact shows a big potential for methane recovery from the coal deposit after carbon dioxide injection.

4 Application of modelling results

One could use data on sorption of CO₂ and CH₄ for rough estimation of CO₂ sequestration potential and methane recovery.

The Morcinek colliery located in the Silesia region is closed. The mining field of this coal mine contains coal of types 34 and 35 accordingly to mark samples in this study. Proven coal

reserves to a level of 950m of depth amount to 54 million of tonnes (operative) and 144 million of tonnes (balance) of coal [15]. The second number represents the space available for the injection of carbon dioxide. Simple calculations on the basis of modeling gives possibility of storage of 2.7 million of tonnes of CO₂ (in operative reserves) and 7.3 million of tonnes in balance reserve. This estimation involves only the expansion and absorption subsystem because probably the self-sealing of deposit appears after CO₂ injection in the butt cleat geological system [5, 8, 17].

Taking into account a typical power station of 309 MW of energy which produces 3 million of tonnes of CO₂ yearly, the capacity of the field will be enough for 3 years of sequestration with assumption of partial CO₂ capturing. Certainly, an incomplete capacity could be accessible for technical operation.

The documented volume of methane amount in the Morcinek coal field is about 2,500 million m³. Estimation of the amount of methane desorbed from the site after injection of the above-mentioned mass of carbon dioxide gives a volume of 200-250 million Nm³ of methane recovered during the entire operation.

A similar procedure could be applied to any mining field of colliery containing coal type identified in this study.

5 Conclusions

The proposed method of the modelling of carbon dioxide and methane gives the possibility of a rough estimation of sequestration capacity of a mining field of closed coal mines together with the possibility of estimation of methane recovery after carbon dioxide injection. Theoretical estimation shows the relatively long time operation (3 years) with the sequestration of carbon dioxide for an exemplary power station. It is obvious that not all the theoretical size can be used for storage of carbon dioxide due to technical reasons.

Another issue is the injection of carbon dioxide into the deep coal layers of over 1000 meters, where the static pressure of overburden exceeds 27 MPa [18], the carbon dioxide exists as a supercritical fluid having a density of 0.468 g/cm³ [19]. Then sorption capacity may reach values ranging from 1.25 to 2 mmol CO₂ per gram of coal. At the same time the presence of water may reduce the value of 1.15 to 1.9 mmol/g. This means the increasing of site capacity 2 times and involves a 5 times bigger mass of coal for CO₂ sequestration. In total, a 10 times bigger storage capacity in this individual mining field.

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References

1. M. S. Masoudian, *Journal of Rock Mechanics and Geotechnical Engineering*, **8** (1), 93-112 (2016)
2. J. Q. Shi, S. Durucan, *Oil & Gas Science and Technology* **60** (3), 547-558 (2005)
3. T. Gentzis, *International Journal of Coal Geology*, **65**: 79-92 (2006)
4. R. Pini, G. Storti, M. Mazzotti, *Adsorption* **17**, 889-900 (2011)
5. C. S. Santarosa, D. Crandall, I. V. Haljasmaa, T-B. Hur, J. J. Fazio, R. P. Warzinski, R. Heemann, J. Marcelo, M. Ketzner, V. N. Romanov, *International Journal of Coal Geology* **106**, 25-34 (2013)
6. M. S. A. Perera, P. G. Ranjith, A. S. Ranathunga, A. Y. J. Koay, J. Zhao, S. K. Choi, *J. Geophys. Eng.* **12**, 90-107 (2015)
7. C. Ö. Karacan, F. A. Ruiz, M. Cotè, S. Phipps, *International Journal of Coal Geology* **86**, 121-156 (2011)
8. A. Mitra, S. Harpalani, S. Liu, *Fuel* **94**, 110-116 (2012)

9. P. Baran, J. Rogozińska, K. Zarębska, S. Porada, *Przemysł Chemiczny*, **93** (12), 2008-2012 (2014)
10. J. Zhang, K. Liu, M. B. Clennell, D. N. Dewhurst, M. Pervukhina, *Fuel* **160**, 309-317 (2015)
11. G. S. Jodłowski, M. Davidová, *Environmental impact and mitigation of carbon dioxide*, Technical University of Košice (2015)
12. G. S. Jodłowski, M. Wójcik, A. Orzechowska-Zięba, *Adsorption*. **22**, 847-854 (2016)
13. J. Milewska-Duda, J. T. Duda, G. S. Jodłowski, M. Kwiatkowski, *Langmuir*. **16**, 7294-7303, (2000)
14. G. S. Jodłowski, P. Baran, M. Wójcik, A. Nodzeński, S. Porada, J. Milewska-Duda, *Langmuir*. **13**, 5732-5735 (2013)
15. <http://kwkmorcinek.pl/index.php?s=zloze> (20.08.2016)
16. <http://www.ppr.pl/artukul.php?id=153107> (22.06.2009)
17. C. F. Rodrigues a,*, C. Laiginhas b, M. Fernandes c, M. J. Lemos de Sousa a, d, M. A. P. Dinis, *Journal of Rock Mechanics and Geotechnical Engineering* **6**, 208-218 (2014)
18. S. Day, R. Sakurovs, S. Weir, *International Journal of Coal Geology* **74**, 203-214 (2008)
19. W. M. Haynes, *CRC Handbook of Chemistry and Physics, 95th Edition*, CRC Press (2014)