

# Kinetic models assessment for swelling of coal induced by methane and carbon dioxide sorption

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**Abstract** The ability of five kinetic equations to describe the sorption kinetics and expansion rate of solid coal samples was investigated. The conducted experiment included the measurements of sorption of methane and carbon dioxide on cuboidal hard coal samples at high pressure using volumetric method. Simultaneously the kinetics of coal sorption induced swelling was monitored. All of the approaches used to fit the experimental sorption and dilatometric data were literature-based equations. Two equations represent the traditional approach for sorption on powder and grain fractions based on the bidisperse gas transport model, and have been used to interpret and quantify the observed gas uptake rates in coal. The other three kinetic equations are the pseudo-second-order kinetic equation, Elovich equation, and stretched exponential (SE) equation. Four of the five equations are suitable to describe the kinetics of methane and carbon dioxide sorption in the porous structure of solid coal samples and the kinetics of coal expansion that accompany the sorption processes. The SE equation gave the best fit to the experimental data.

**Keywords** Hard coal · Sorption kinetics · Methane sorption · Carbon dioxide sorption · Coal swelling

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## 1 Introduction

Ecological issues and prospective economic aspects have resulted in increasing interest in the sequestration of carbon dioxide and the enhanced coal bed methane recovery (ECBM) process, that is, recovery of methane from carboniferous deposits with simultaneous CO<sub>2</sub> sequestration (Dutka et al. 2013; Jodłowski et al. 2007; Jodłowski 2008; Kaszuba and Janecky 2013; Wdowin et al. 2014a, b). This constitutes one method to lower the emission of carbon dioxide. Determination and clear understanding of the relations between the range of expansion/contraction of hard coal and the volume of gas sorbed in its porous structure in coal–methane, coal–carbon dioxide, and coal–gas mixture (CH<sub>4</sub> and CO<sub>2</sub>) systems are important issues in carbon dioxide sequestration and recovery of methane from carboniferous formations. Fundamental issues that need to be investigated are changes caused by coal–gas (CH<sub>4</sub>, CO<sub>2</sub>) interactions within a coal bed and the underlying mechanisms, as well as analytical and numerical methods to describe such changes (Czerw 2011).

Mine gases are deposited in coal beds in different forms: (1) adsorbed in micropores and on the surface of larger pores; (2) absorbed in the coal molecular structure; (3) as free gas in fissures and larger pores, which becomes significant at higher sorbate pressures; and (4) dissolved in deposit waters (Mastalerz et al. 2004; Zarębska and Ceglarska-Stefańska 2008). For the two main components of mine gas, methane has lower diffusivity, which is why its sorption rate is lower than that of carbon dioxide (Busch et al. 2004; Clarkson and Bustin 1999a, b; Cui et al. 2004). Investigation of solid hard coal samples has shown not only the sorption process, but also sorption-induced swelling of the sorbent caused by vapors and gases. Research into coal has led to the conclusion that coal is a biporous, transport-

sorption system in which high pressure of gases causes compression of microporous regions and expansion of macropores. Expansion of microporous coal regions induced by gas sorption causes transport pores to narrow and the in situ system permeability of the bed to decrease (Pan and Connell 2007; Seewald and Klein 1986). The majority of research indicates that there is a linear relation between coal expansion and the volume of gas sorbed in its structure (Baran et al. 2015; Bustin et al. 2008; Chikatarla et al. 2004; Cui et al. 2007; Czerw 2011; Harpalani and Chen 1995; Levine 1996; Ottinger et al. 2008; Robertson and Christiansen 2005; St. George and Barakat 2001). However, there are also studies that suggest that the sorption processes and range of contingent strains are not linearly dependent (Ceglarska-Stefanska et al. 2007; Pan and Connell 2007).

Because the majority of studies suggest that the swelling of coal is approximately proportional to the volume of sorbed gas, herein we assume that it might be possible to use the same approach to determine equations that provide a mathematical description of the kinetic curves for both sorption and swelling. Sorption kinetics concerns the time dependence or rate of reactions, and it is usually described in terms of a mathematical relationship between the amount of sorbed substance (equivalent to weight gain or volume of accumulated agent) and time. Unipore and bidisperse gas transport models have been used to interpret and quantify the observed gas uptake rates in coal with equations of different complexity (Busch and Gensterblum 2011). The unipore model is based on the solution to Fick's second law for spherical symmetric flow. It should be noted that the model assumes spherical homogeneous coal particles with the same radius and a smooth surface, a homogeneous pore structure, isothermal conditions, and that the diffusion coefficient is independent of the concentration and location in the coal particle (Busch et al. 2004; Charrière et al. 2010; Clarkson and Bustin 1999b; Pan et al. 2010; Pone et al. 2009). Ruckenstein et al. (1971) developed a bidisperse sorption/diffusion model that can be used for coals characterized by two distinct pore systems. The model defines these systems as an agglomeration of many microporous spheres contained in macropores. The model assumes a linear isotherm in both macro- and microspheres and a step change in the boundary concentration at the start of a sorption step (Busch et al. 2004; Clarkson and Bustin 1999b; Cui et al. 2004; Siemons et al. 2007; Shi and Durucan 2003a, b; Yi et al. 2008). However, CO<sub>2</sub> and CH<sub>4</sub> sorption isotherms are typically non-linear for natural coal, which limits the applicability of the model (Busch and Gensterblum 2011). Although it is not generally confirmed, unipore models seem to better represent the sorption kinetics of high rank coals (medium-volatile bituminous coal to anthracite) while bidisperse models

better represent low rank coals. This is in agreement with the observation that micropores increase and mesopores decrease with coal rank (Busch and Gensterblum 2011).

In this study, we evaluated the ability of a variety of sorption kinetics equations to describe not only the sorption kinetics but also the rate of expansion/contraction of hard coal in coal–carbon dioxide and coal–methane systems.

## 2 Experimental methods

The sorption of methane and carbon dioxide on cuboidal hard coal samples was investigated at high pressure. Basic coal samples (high-volatile bituminous C rank according to ECE-UN In Seam Coal Classification, type 32.2 according to Polish standard PN-82/G-97002) were obtained from the Brzeszcze-Silesia mine. A coal sample with dimensions of 20 mm × 20 mm × 40 mm was cut out of the basic coal in such a way that the 20 mm × 20 mm walls were parallel to the bedding plane. The results of analysis performed on the basic coal samples are shown in Table 1. The two coal samples are designated CH<sub>4</sub> and CO<sub>2</sub> according to the gas used in the sorption experiment.

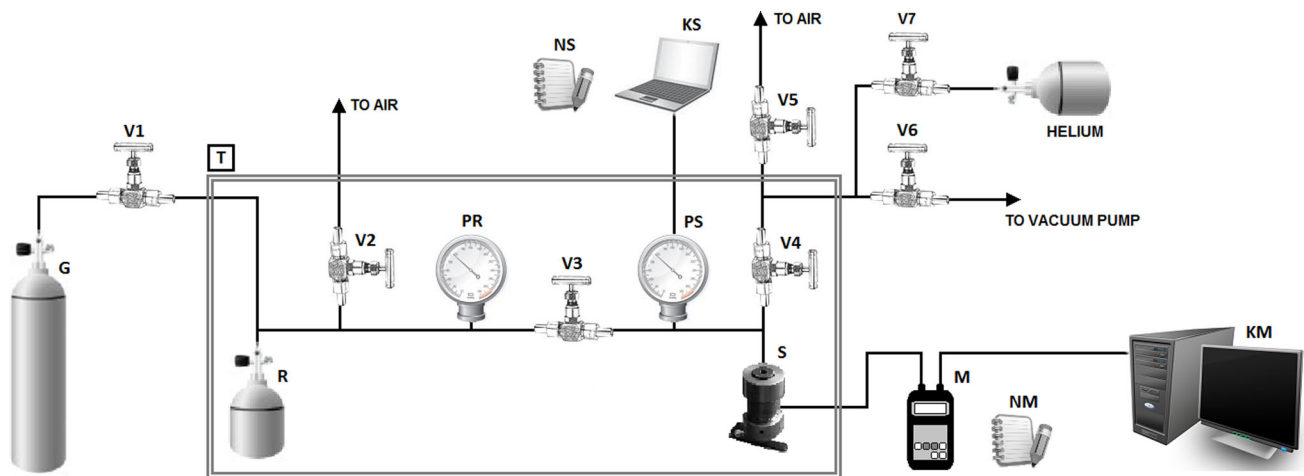
At the same time as the sorption kinetics were monitored, changes of the sample's overall dimensions accompanying the sorption processes were measured. Experiments were performed using the apparatus and test procedures described by Majewska and Ceglarska-Stefanska (2009). The experimental set-up consisted of two individual units: (1) a gas sorption apparatus using the volumetric method (pressure meter MKS BARATRON 722A with a measuring range of 0–4.0 MPa and measurement accuracy ±0.001 MPa) and (2) a strain meter to measure changes in the external dimensions of the samples induced by gas sorption and pressure (electrical resistance bridge, type SGM-1C81, constructed in the Strata Mechanics Research Institute of The Polish Academy of Science, measuring the range of linear strain ~4 ‰, measurement accuracy 0.001 ‰, with domestic production resistance-type paper strain gauge type RL120) (Fig. 1). The whole apparatus was thermostabilized, which enabled measurements to be taken at a constant temperature of 298 K. The experimental procedure included degassing of the sorption apparatus and sample (vacuum 10<sup>-5</sup> Pa) and immersion in a helium bath (10 kPa). This was performed to remove possible interfering sorbed gases and vapors, including water, from the porous coal structure. The kinetics of methane and carbon dioxide sorption were determined from the results of the experiments based on the pressure changes in the sample cell. The kinetics of the induced strain perpendicular ( $\varepsilon_T$ ) and parallel ( $\varepsilon_L$ ) to the bedding plane were calculated, from which the kinetics of the volumetric strain ( $\varepsilon_V$ ) was calculated using the equation  $\varepsilon_V = \varepsilon_T + 2\varepsilon_L$ .

**Table 1** Specification of coal samples: proximate and ultimate analysis, maceral composition, mineral matter content, and vitrinite reflectance (CH<sub>4</sub>: Czerw et al. 2010; CO<sub>2</sub>: Czerw 2011)

Coal*	W <sup>a</sup> (%)	A <sup>a</sup> (%)	C <sup>a</sup> (%)	C <sup>daf</sup> (%)	H <sup>a</sup> (%)	N <sup>a</sup> (%)	S <sup>a</sup> (%)	R <sup>o</sup> (%)	d <sub>R</sub> 10 <sup>3</sup> (kg/m <sup>3</sup> )	d <sub>A</sub> 10 <sup>3</sup> (kg/m <sup>3</sup> )
Proximate and ultimate analysis										
CH <sub>4</sub>	2.3	4.09	77.53	82.82	4.56	1.43	0.22	0.77	1.345	1.311
CO <sub>2</sub>	1.52	11.23	72.21	82.76	4.31	1.19	0.37	0.78	1.379	1.355
Coal*	Telinite (%)	Collotelinite (%)	Vitrodetrinite (%)	Collodetrinite (%)	Corpogelinite (%)	Gelinite (%)	Total vitrinite (%)	Sporinite (%)	Resinite (%)	Liptodetrinite (%)
Coal macerals and mineral matter content										
CH <sub>4</sub>	2.8	33.7	0.3	9.6	0.3	1.7	48.4	7.8	0.5	1.6
CO <sub>2</sub>	3.0	24.2	1.3	9.2	1.0	2.5	41.2	6.5	2.1	2.3
Coal*	Cutinite (%)	Total liptinite (%)	Fusinite (%)	Semifusinite (%)	Macrinite (%)	Micrinite (%)	Funginite (%)	Inertodetrinite (%)	Total inertinite (%)	Mineral matter (%)
Coal macerals and mineral matter content										
CH <sub>4</sub>	0	9.9	15.8	11.2	1.1	0.9	0.2	8.4	37.6	4.1
CO <sub>2</sub>	0	10.9	14.2	18.6	2.6	1.2	śl.	8.4	45.0	2.9

W<sup>a</sup> moisture content, A<sup>a</sup> ash content, C<sup>a</sup> content of element C, air-dried basis, C<sup>daf</sup> content of element C, dry-ash-free basis, H<sup>a</sup> content of element H, air-dried basis, N<sup>a</sup> content of element N, air-dried basis, S<sup>a</sup> content of element S, air-dried basis, R<sup>o</sup> vitrinite reflectance, d<sub>R</sub> true density, d<sub>A</sub> apparent density

\* The names of the samples correspond to the gas used in the sorption experiments



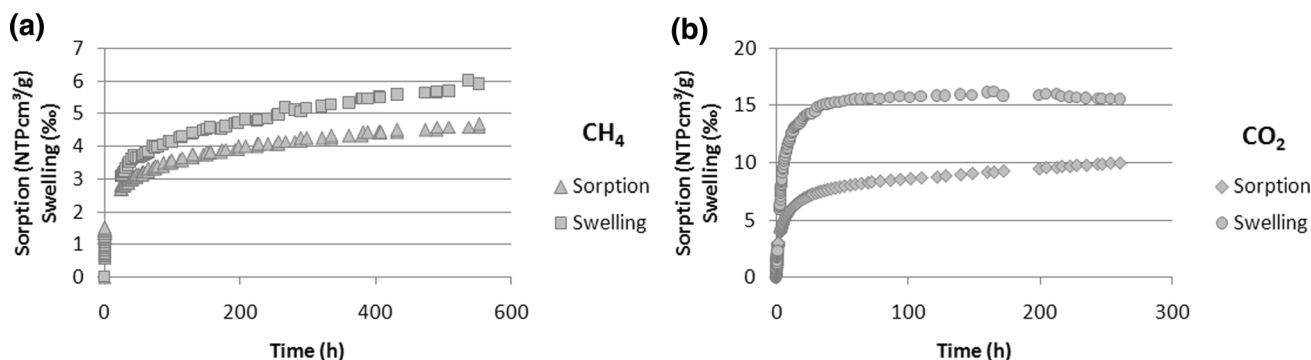
**Fig. 1** Schematic diagram of the experimental setup. G gas supply cylinder, R reference cell, S sample cell, M strain meter, T temperature-controlled environment, PS, PR pressure transducers, V1, V2,

V3, V4, V5, V6, V7 pressure valves, KS, KM PC-based data recording units, NS, NM hand-written data records

### 3 Results

Figure 2 shows the kinetic curves of sorption of carbon dioxide and methane in the porous structure of the coal samples and the kinetic curves of coal expansion that accompany the sorption processes. The x axis represents

the time of contact between the sample and the sorbate [Time (h)]. The y axis shows the volumetric swelling of coal [Swelling (%)], which corresponds to the amount of gas (centimeter cubed at Normal Temperature and Pressure conditions per gram) sorbed in the porous coal structure [Sorption (NTPcm<sup>3</sup>/g)].



**Fig. 2** Kinetics of gas sorption and swelling for **a** CH<sub>4</sub> (Czerw et al. 2010) and **b** CO<sub>2</sub>. The experimental data are given symbols corresponding to the gas and the process that they represent: *triangle*

for CH<sub>4</sub> sorption, *diamond* for CO<sub>2</sub> sorption, *square* for CH<sub>4</sub>-sorption-induced swelling, and *circle* for CO<sub>2</sub>-sorption-induced swelling

## 4 Discussion

### 4.1 Carbon dioxide and methane sorption kinetics

Five sorption kinetic equations were investigated. The approach of Busch et al. (2004) is based on the bidisperse sorption/diffusion model and describes the gas sorption kinetics as a linear combination of two first-order rate functions:

$$Y_{\text{residual}}(t) = Y' \exp(-k't) + Y'' \exp(-k''t) \quad (1)$$

The normalized equilibration curves are expressed in terms of the relative residual (unoccupied) sorption amount  $Y_{\text{residual}}$  ( $Y_{\text{res}}$ ) as a function of time with different rate constants  $k'$  and  $k''$ , and normalized sorption at equilibrium  $Y'$  and  $Y''$  (with  $Y'' = 1 - Y'$ ) because the authors classify the transport as fast and slow. In contrast to the unipore model, this equation provides a perfect fit of the experimental data using a simple semi-empirical approach (Busch et al. 2004).

The expansion kinetics can be described by the equation:

$$E_{\text{residual}}(t) = E' \exp(-k't) + E'' \exp(-k''t) \quad (2)$$

where  $E_{\text{residual}}$  ( $E_{\text{res}}$ ) is the relative residual expansion, which is the potential relative swelling described by  $E_{\text{res}}(t) = [E(t) - E_{\text{eq}}] / (E_0 - E_{\text{eq}})$ ,  $k'$  and  $k''$  are different rate constants, and the parameters  $E'$  and  $E''$  represent expansion at equilibrium (with  $E'' = 1 - E'$ ). For the purpose of this analysis, the values of the equilibrium sorption amount [ $V_{\text{eq}}$  (NTPcm<sup>3</sup>/g)] and equilibrium expansion [ $E_{\text{eq}}$  (%)] were calculated.

Following the approach of Siemons et al. (2007), an equation based on the bidisperse sorption/diffusion model composed of the sum of two exponentially decreasing functions was used. This procedure is similar to that presented by Busch et al. (2004) and includes splitting the

sorption contributions into a fast and a slow process to give the double-exponential (DE) equation:

$$\left(\frac{P}{Z}\right)(t) = A' \exp\left(-\frac{t}{t'}\right) + A'' \exp\left(-\frac{t}{t''}\right) + P_{\text{eq}} \quad (3)$$

The changes of pressure  $P$  divided by compressibility factor  $Z$  ( $P/Z$ ) are a measure of the sorption progress. The pressure decay curves are characterized by the intensities  $A'$  and  $A''$  (with  $A'' = (P_0 - P_{\text{eq}}) - A'$ ) and two characteristic times:  $t'$  for the fast process and  $t''$  for the slow process.  $P_{\text{eq}}$  is the pressure offset of the individual pressure step (equilibrium pressure) and  $t$  (h) represents the experimental time. The equation for the expansion kinetics is:

$$E_{\text{remaining}}(t) = A' \exp\left(-\frac{t}{t'}\right) + A'' \exp\left(-\frac{t}{t''}\right) + E_{\text{eq}} \quad (4)$$

where  $E_{\text{remaining}}$  is the remaining potential expansion,  $E_{\text{remaining}} = E_{\text{eq}} - E(t)$ , and  $A'' = (E_0 - E_{\text{eq}}) - A'$ . A similar equation was developed by Gawor and Skoczylas (2014), although the equation is based on the heat conductivity equation and involves measurements of the heat balance of a coal-coated thermometer during the gas sorption process.

Marecka and Mianowski (1993) proposed an empirical kinetic pseudo-second-order rate equation (PSOE) under isothermal–isobaric conditions based on chemometric analysis of kinetic equations describing the diffusion process in the hard coal–gas system. The mathematical form of the PSOE was first proposed by Blanchard et al. (1984) to describe the kinetics of heavy metal removal by natural zeolites. It is the most commonly used equation to describe sorption kinetic data (Płaziński et al. 2013; Marczewski et al. 2013). The general form of the differential equation describing the rate of fractional uptake given by Marecka and Mianowski (1993) is:

$$\frac{dy}{dt} = k \left( \frac{y_{\infty} - y}{y_{\infty}} \right)^2 \quad (5)$$

The equation is characterized by two parameters: the kinetic constant  $k$  as the rate constant of the sorption process and the parameter  $y_\infty$ , which is a measure of the distance from the state of sorption equilibrium and is called the limit parameter. For the initial conditions  $t = 0$  and  $y = 0$ , Eq. (5) leads to:

$$y = y_\infty \frac{kt}{y_\infty + kt} \tag{6}$$

where  $y$  is the sorption progress  $y = a/a_{eq}$ . The authors showed that application of the proposed equation for the description of the kinetics of CO<sub>2</sub> and CH<sub>4</sub> sorption on coal was justified. For the purpose of this analysis, Eq. (6) was transformed to Eqs. (7) and (8) to include the sorption amount rate and swelling rate:

$$V(t) = V_{eq} \frac{kt}{1 + Akt} \tag{7}$$

$$E(t) = E_{eq} \frac{kt}{1 + Akt} \tag{8}$$

where parameter  $A$  is substituted for  $1/y_\infty$ . The values of the equilibrium sorption amount [ $V_{eq}$  (NTPcm<sup>3</sup>/g)] and equilibrium expansion [ $E_{eq}$  (%)] have been previously calculated.

The Elovich equation (Aharoni and Suzin 1982; Aharoni and Tompkins 1970) corresponds to chemisorption. Because the sorbed amount has no maximum value it goes to infinity and should be avoided. However, it was adapted for the purpose of this analysis in its integrated forms:

$$V(t) = \frac{1}{B} \ln(ABt + 1) \tag{9}$$

$$E(t) = \frac{1}{B} \ln(ABt + 1) \tag{10}$$

These equations are characterized by the two parameters  $A$  and  $B$ .

The stretched exponential (SE) equation was developed as a global kinetic equation by Kolmogorov, Erofeev, Kozeeva, Avrami, and Mampel, and it is called the KEKAM equation (Avrami 1939; Brouers and Sotolongo-Costa 2006). For the purpose of this analysis, the following forms were used:

$$V(t) = V_{eq} \left\{ 1 - \exp \left[ -(kt)^A \right] \right\} \tag{11}$$

$$E(t) = E_{eq} \left\{ 1 - \exp \left[ -(kt)^A \right] \right\} \tag{12}$$

which are characterized by parameter  $A$  and rate coefficient  $k$ . The values of the equilibrium sorption amount [ $V_{eq}$  (NTPcm<sup>3</sup>/g)] and equilibrium expansion [ $E_{eq}$  (%)] have been previously calculated.

## 4.2 Analysis results

Figures 3, 4, 5, 6, and 7 show scatterplots of the application of the kinetic equations. Additional Figs. S1–S5, analogues to Figs. 3, 4, 5, 6, and 7, are given in Online Resource 1. In Figs. S1–S5  $t^{1/2}$  time scale was used instead of linear time scale.

The first approach using the equation of Busch et al. based on two combined first-order rate functions gives a reasonable fit to the experimental data for CH<sub>4</sub> and CO<sub>2</sub> sorption and swelling, but the approximation seems to be better in the case of the expansion measurements (Fig. 3). The residual (unoccupied) relative sorption amount ( $Y_{residual}$ ) (Fig. 3a, b) or the amount of residual expansion ( $E_{residual}$ ) (Fig. 3c, d) is shown on the  $y$  axis and the  $x$  axis is time (h).

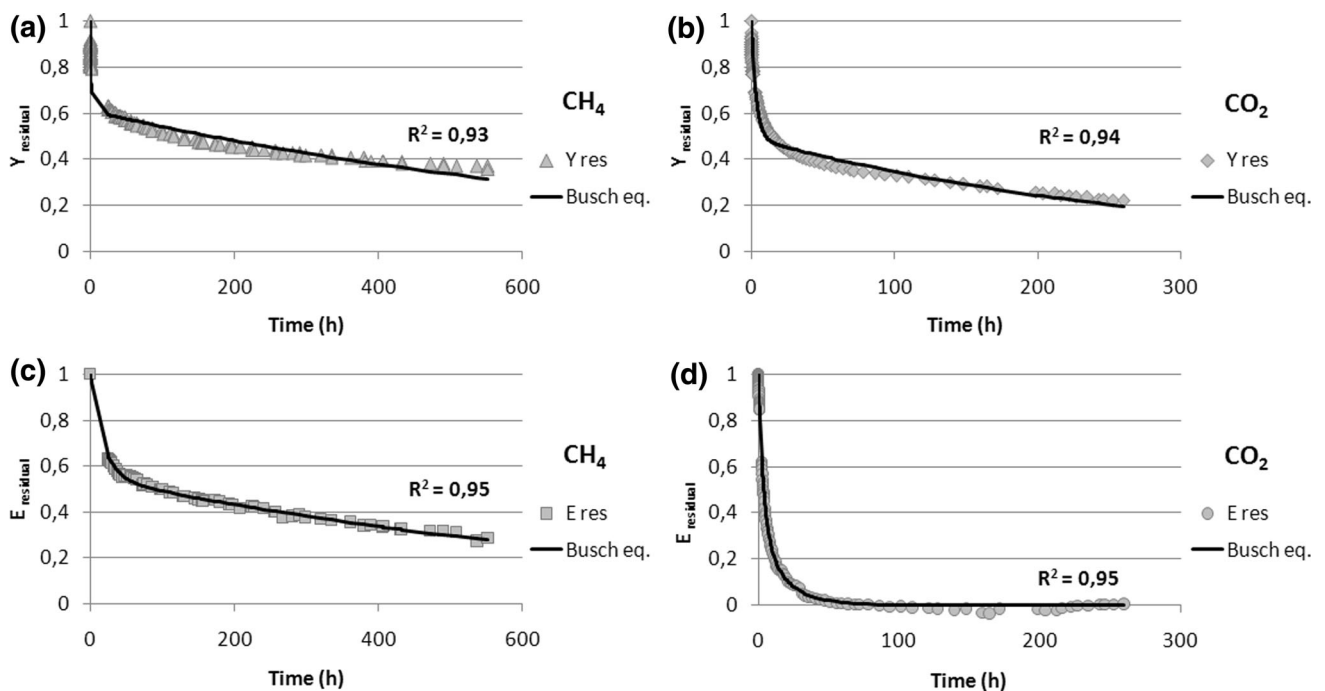
The equation proposed by Siemons et al. (2007) is the relationship between the pressure [ $P/Z$  (MPa)] (Fig. 4a and b) or the amount of remaining expansion ( $E_{remaining}$ ) (Fig. 4c, d) and time (h). Figure 4 shows that the pressure decay curves for both CH<sub>4</sub> and CO<sub>2</sub> sorption and the swelling behavior are well-fitted by the Siemons equation, and the fit is better than for the Busch equation (Fig. 3). However, the difference between the experimental data and the fitted results for the swelling behavior with CO<sub>2</sub> after about 200 h makes this equation inadequate (Fig. 4d).

The fitting results of the PSOE, Elovitch equation, and SE are shown in Figs. 5, 6, and 7, respectively. In these figures, the  $y$  axis is the amount of sorbed gas [Sorption (NTPcm<sup>3</sup>/g)] for parts a and b, and the volumetric swelling of coal [Swelling (%)] for parts c and d. The  $x$  axis is time (h).

The PSOE shows good agreement with the experimental data obtained by Marecka and Mianowski (1993). However, application of the proposed equation to the experimental data of sorption of CH<sub>4</sub> and CO<sub>2</sub> is unsuitable (Fig. 5a, b), it is not suitable for the swelling kinetics (Fig. 5c, d). We calculated the equilibrium sorption amount [ $V_{eq}$  (NTPcm<sup>3</sup>/g)] and equilibrium expansion [ $E_{eq}$  (%)]. However, the kinetic PSOE underestimates these values. The conclusion is that the PSOE might be unsuitable for experiments with solid samples, in contrast to traditional research of sorption on powders and grain fractions.

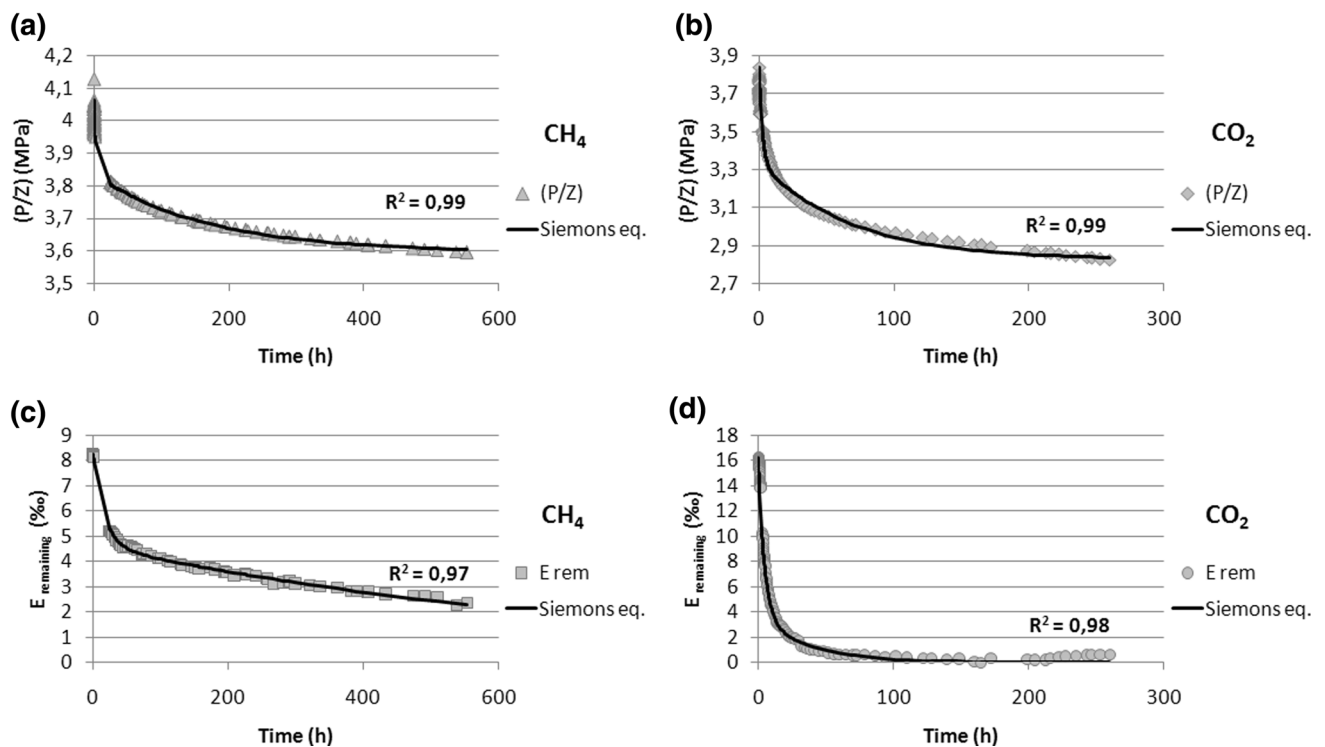
From Fig. 6, the Elovitch equation is able to accurately describe the sorption kinetic of CH<sub>4</sub> and CO<sub>2</sub> as well as the CH<sub>4</sub>-induced swelling behavior of coal (Fig. 6a–c). This equation shows good agreement with experimental data, except for the CO<sub>2</sub>-induced swelling behavior (Fig. 6d).

Figure 7 shows the results of applying the SE kinetic equation. The fitted results are in excellent agreement with the test results. This equation is the most promising



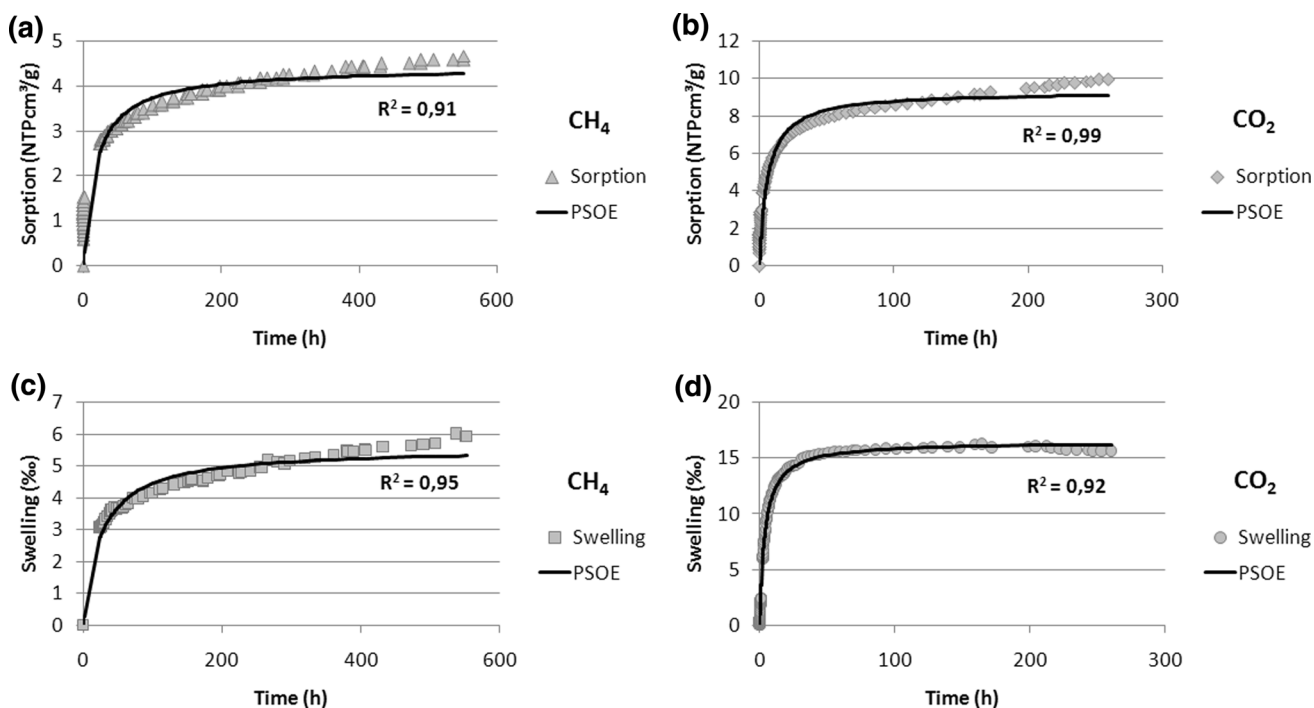
**Fig. 3** Application of the Busch equations to the kinetics for **a** CH<sub>4</sub> and **b** CO<sub>2</sub> sorption (Eq. 1), and the sorption-induced coal swelling kinetics for **c** CH<sub>4</sub> and **d** CO<sub>2</sub> (Eq. 2). The residual values are given symbols: *triangle* for CH<sub>4</sub> sorption, *diamond* for CO<sub>2</sub> sorption, *square*

for CH<sub>4</sub>-sorption-induced swelling, and *circle* for CO<sub>2</sub>-sorption-induced swelling. The *solid line* corresponds to the results of Busch equation application



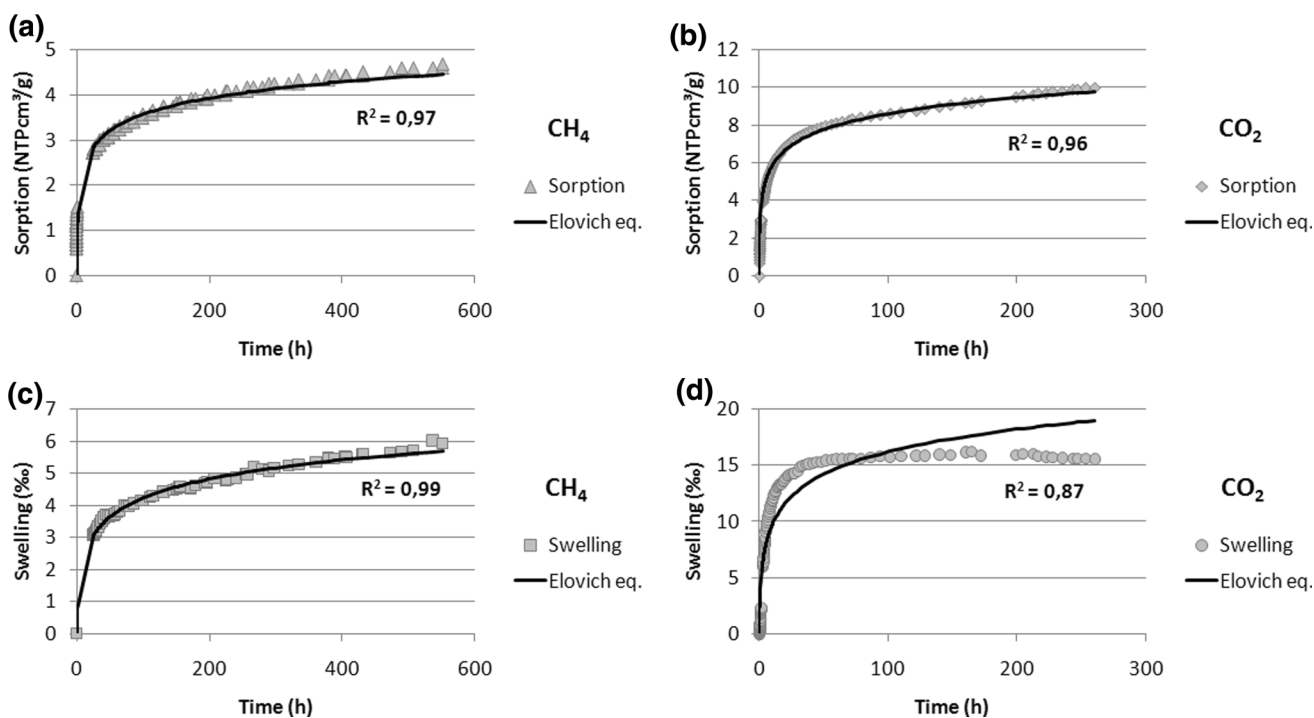
**Fig. 4** Application of the Siemons equations to the kinetics for **a** CH<sub>4</sub> and **b** CO<sub>2</sub> sorption (Eq. 3), and the sorption-induced coal swelling kinetics for **c** CH<sub>4</sub> and **d** CO<sub>2</sub> (Eq. 4). The remaining values are given symbols: *triangle* for CH<sub>4</sub> sorption, *diamond* for CO<sub>2</sub> sorption, *square*

for CH<sub>4</sub>-sorption-induced swelling, and *circle* for CO<sub>2</sub>-sorption-induced swelling. The *solid line* corresponds to the results of Siemons equation application



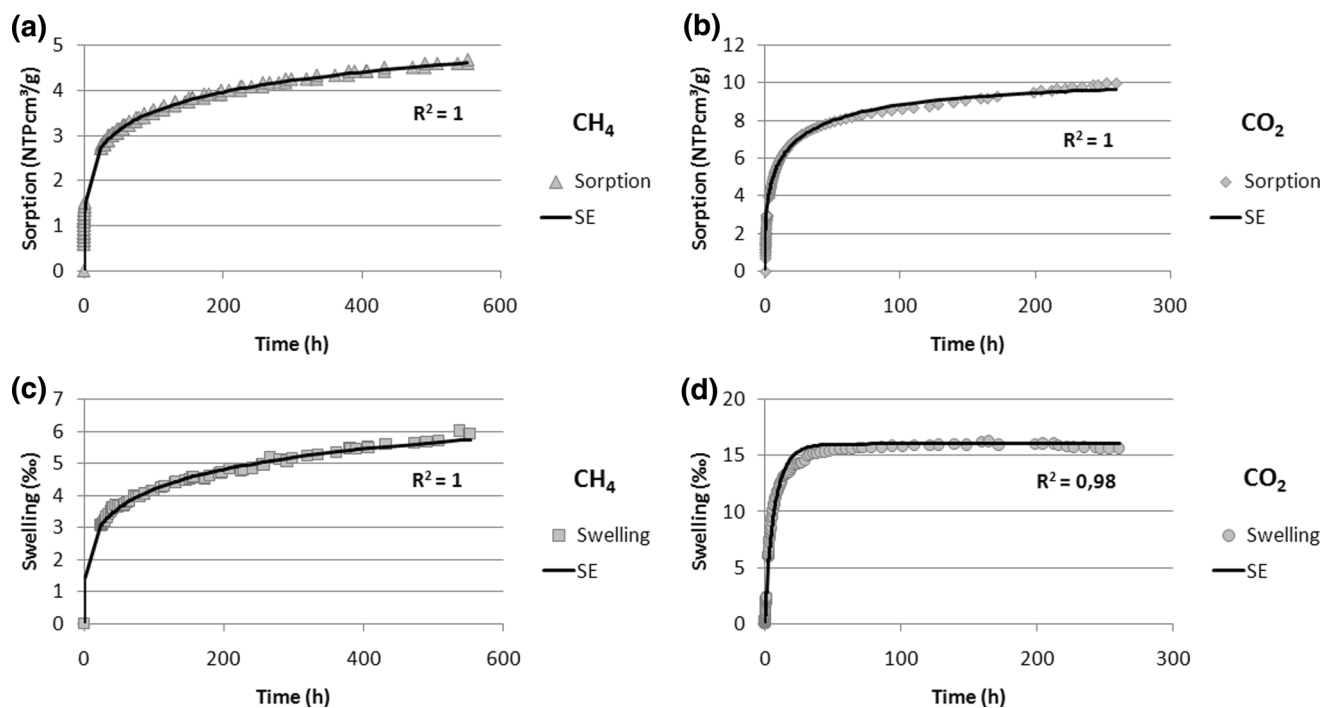
**Fig. 5** Application of the PSOEs to the kinetics for **a** CH<sub>4</sub> and **b** CO<sub>2</sub> sorption (Eq. 7), and the sorption-induced coal swelling kinetics for **c** CH<sub>4</sub> and **d** CO<sub>2</sub> (Eq. 8). The experimental data are given symbols: *triangle* for CH<sub>4</sub> sorption, *diamond* for CO<sub>2</sub> sorption, *square* for CH<sub>4</sub>-

sorption-induced swelling, and *circle* for CO<sub>2</sub>-sorption-induced swelling. The *solid line* corresponds to the results of PSOEs application



**Fig. 6** Application of the Elovitch equations to the kinetics for **a** CH<sub>4</sub> and **b** CO<sub>2</sub> sorption (Eq. 9), and the sorption-induced coal swelling kinetics for **c** CH<sub>4</sub> and **d** CO<sub>2</sub> (Eq. 10). The experimental data are given symbols: *triangle* for CH<sub>4</sub> sorption, *diamond* for CO<sub>2</sub> sorption,

*square* for CH<sub>4</sub>-sorption-induced swelling, and *circle* for CO<sub>2</sub>-sorption-induced swelling. The *solid line* corresponds to the results of Elovitch equation application



**Fig. 7** Application of the SE equations to the kinetics for **a** CH<sub>4</sub> and **b** CO<sub>2</sub> sorption (Eq. 11), and the sorption-induced coal swelling kinetics for **c** CH<sub>4</sub> and **d** CO<sub>2</sub> (Eq. 12). The experimental data are given symbols: *triangle* for CH<sub>4</sub> sorption, *diamond* for CO<sub>2</sub> sorption,

*square* for CH<sub>4</sub>-sorption-induced swelling, and *circle* for CO<sub>2</sub>-sorption-induced swelling. The *solid line* corresponds to the results of SE equation application

approach to fit the experimental results of both the sorption processes and expansion phenomena of solid coal samples.

## 5 Conclusions

In this study, five approaches were used to fit experimental sorption and dilatometric data of gas sorption to coal. For two equations based on the bidisperse gas transport model, the equation proposed by Busch et al. (2004) is better to interpret and quantify observed gas uptake rates in coal than the equation proposed by Siemons et al. (2007). The PSOE of Marecka and Mianowski (1993) is unsuitable for the data. The Elovich equation fits the results obtained in this study well, because the sorption and sorption-induced expansion processes were still in progress and the problem of a lack of a maximum sorbed amount value in the equation did not occur. However, because the function goes to infinity it should be avoided. The SE equation gives the best fit and is in very good agreement with the experimental results.

We believe that four out of the five equations investigated in this study are suitable to fit the kinetic curves of the accumulation of methane and carbon dioxide in the porous structure of coal and the kinetic curves of coal expansion that accompany the sorption processes. The

exceptions are the PSOE equation and the Elovich equation to fit CO<sub>2</sub>-sorption-induced swelling of coal. The best fit to the experimental data was achieved using the SE equation.

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