Sorption rate of CH_4 and CO_2 in coal at different pressure ranges

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Abstract. The aim of this study was to verify the dynamic factor, that is the diffusion rate, which can directly affect the efficiency of CO_2 injection and as a consequence – storage. A manometric setup was used for experiments on two hard coals from Upper Silesian Coal Basin in Poland. A model combining two firs-order rate functions with different rate constants was used to plot normalized equilibration curves. Diffusion curves were plotted at three pressure ranges 5-6 MPa, 3.5-4 MPa and 1.5-2 MPa. Result show that fast adsorption rate is higher at 5.5-6 MPa than at lower pressure range with highest fast adsorption rate fraction both for CH_4 and CO_2. Lower (1.5-2 MPa) pressure range allows achieving sorption equilibrium in less time for both gases. Diffusion rates are lower for CO_2 than for methane the CH_4 desorption rate has a slight impact on the CO_2 adsorption and as a consequence CO_2 storage capacity.

1. Introduction
Recent regulations related to carbon dioxide emission force power companies, cement and metal manufacturers to seek for different methods of CO_2 emission reductions. Although there are numerous technologies which can be used to reduce CO_2 emissions there is still lack of sufficient economic factor that can foster their implementation and meet targets of 2050 Energy roadmap in European Union [1]. One of the solutions that could work for fossil fuel based economies is the Carbon Capture and Storage (CCS). In this technology CO_2 is captured in stationary emission source, transported and permanently stored underground in geological traps. This technology is well known and although not widely implemented to date, it has a huge potential and when taking into consideration the dominant role that fossil fuels continue to play in primary energy consumption, the deployment of CCS technologies is becoming increasingly urgent [2]. Concerning Europe, a considerable amount of studies has been conducted about the implementation of CCS in unmineable coal seams, with particular attention to Poland (particularly in the Upper Silesian Basin) where there are still considerable amounts of Coalbed Methane reservoirs. In order to assess CO_2 storage capacity the following parameters have to be taken into consideration:
- Sorption capacity of coal (Langmuir parameters)
- Water saturation of coal
- Coal porosity

In order to assess the dynamic properties of CBM reservoir, other parameters, such as permeability diffusion coefficient, are needed. In the previous study, a petrophysical static model was applied in order to assess the total storage capacity of coalbed [3]. This research is focused on the dynamic factor, that is the sorption rate which can directly affect the efficiency of CO_2 injection and as a consequence – storage.

2. Materials and methods

In the study two coal samples from the Upper Silesia Coal Basin (USCB) in Poland were used. They represented two types of steam coal i.e. good quality coal with low ash content (Coal A) and low quality coal with high ash content (Coal B). Experiments were carried in a manometric sorption setup. Detailed description of the setup and experimental procedure is given in [3,4]. Proximate analysis of coals are presented in Table 1.

Table 1. Properties of coal used in the study.

Parameter	Coal A	Coal B
Ash content, %	4.66	11.33
Moisture content (as received), %	0.2	2.1
Moisture content (air dried), %	1.38	7.46
Higher heating value, KJ/kg	33376	22060

The diffusion curves of gas in coal can be assumed as equal both in adsorption and desorption process [5,6]: therefore, diffusion curves of CO_2 can give a reference for the variation of the stored quantities in time, while the ones of methane can give a reference for the variation of the produced quantities. The diffusion processes of methane and carbon dioxide have been analyzed at different pressure levels to assess possible difference and changings in the process due to the injection pressure, which is the initial pressure of the diffusion process. Three pressure ranges for carbon dioxide and methane were selected i.e.: 5-6 MPa, 3.5-4 MPa and 1.5-2 MPa. This indicates the pressure step at which adsorption starts. The time at which the equilibrium was attained varied from 0.6 days up to almost two weeks.

To estimate diffusion rate, a numerical diffusion model proposed by Busch and Gensterblum [5] combining two firs-order rate functions with different rate constants was used. The model expresses the quantity of gas diffused at a certain moment of time in terms of the residual (unoccupied) sorption capacity $Q_{residual}(t)$:

$$Q_{residual}(t) = \frac{P(t) - P_\infty}{P_0 - P_\infty}$$

Where:
$P(t)$ - system pressure at time t;
P_∞- system equilibrium pressure; and
P_0- initial system pressure.

The formula above allows the calculation of $Q_{residual}(t)$ for discrete values of pressure and time derived from experimental data. To extend the calculation of $Q_{residual}(t)$ and create a continuous function, the model proposes to calculate the residual sorption capacity as:

$$Q_{residual}(t) = Q_0' \times \exp(-k' \times t) + Q_0'' \times \exp(-k''t)$$

Where:
Q_0'- fraction of fast sorption;
k'- fast sorption first order rate constant;
Q_0'' - fraction of slow sorption;
k''- slow sorption first order rate constant.

During diffusion, two characteristic speed rates are present: the first one, which is the fastest, occurs in the first periods of time of the process, while the second one, which is slower, rules the diffusion in the following time. Fast and slow sorption fractions therefore refer to the fractions of gas adsorbed during these two sorption processes. The two first rate constant are used instead to calculate the time of fast and slow sorption:

$$t_{Q_0''''} = \frac{\ln(2)}{k''''}$$

The calculation of the fractions and rate constants value is obtained from the minimisation of the standard deviations between $Q_{residual}(t)$ values calculated with the first formula from the sorption experimental data.

3. Results and discussion

In Table 2 results of diffusion rate calculated with numerical model for the two types of coal at different pressure ranges have been shown.

Table 2. Results of CH_4 and CO_2 diffusion rate calculation at different pressure range.

	Pressure Range	Coal sample	Fast sorption fraction	Slow sorption fraction	Fast sorption time (s)	Slow sorption time (s)	Diffusion time (s)	Diffusion time (d)
CH_4	5.5-6 MPa	A	39%	61%	417	20090	607000	7.0
		B	48%	52%	65	13269	398000	4.6
	3.5-4 MPa	A	22%	75%	439	39138	1195000	13.8
		B	41%	59%	340	35322	1065000	12.3
	1.5-2 MPa	A	29%	71%	530	18214	447000	5.2
		B	46%	54%	378	14887	447000	5.2
CO_2	5.5-6 MPa	A	52%	48%	216	1712	52000	0.6
		B	61%	39%	382	8531	252000	2.9
	3.5-4 MPa	A	53%	47%	477	4315	129000	1.5
		B	69%	31%	449	12750	373000	4.3
	1.5-2 MPa	A	41%	59%	404	4939	149000	1.7
		B	53%	47%	254	4035	121000	1.4

Results show that for coal A the fast adsorption rate is higher at 5.5-6 MPa than at lower pressure range with highest fast adsorption rate fraction both for CH_4 and CO_2, 39% and 52% respectively. The 1.5-2 MPa pressure range allows achieving sorption equilibrium in less time for both gases. At higher pressure (5.5-6 MPa) it is possible to achieve a larger amount of gas stored in a comparable amount of time (7 days against 5.2 days) for sample A and CH_4. Comparison of normalized CH_4 and CO_2 sorption equilibration rates for coal A and B are shown in Figure 1, 2, 3 and 4.
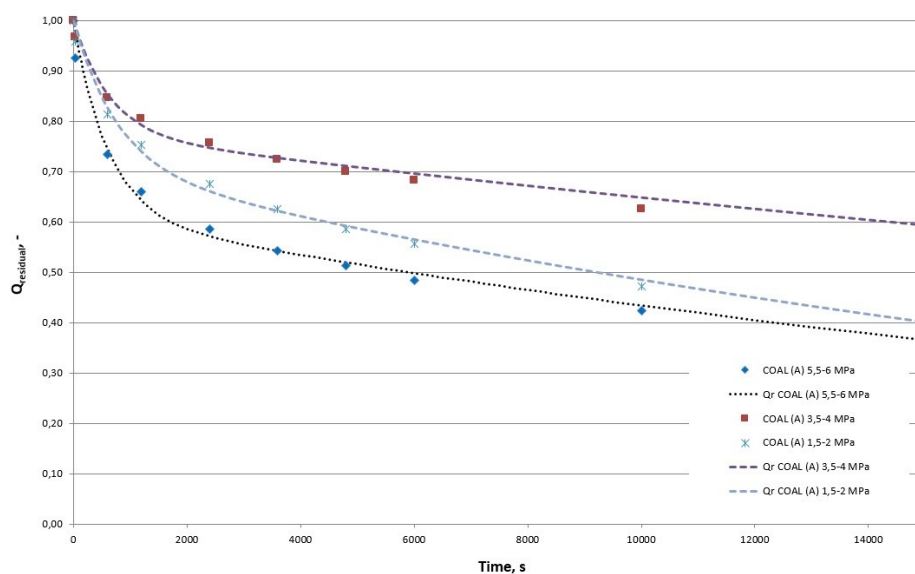
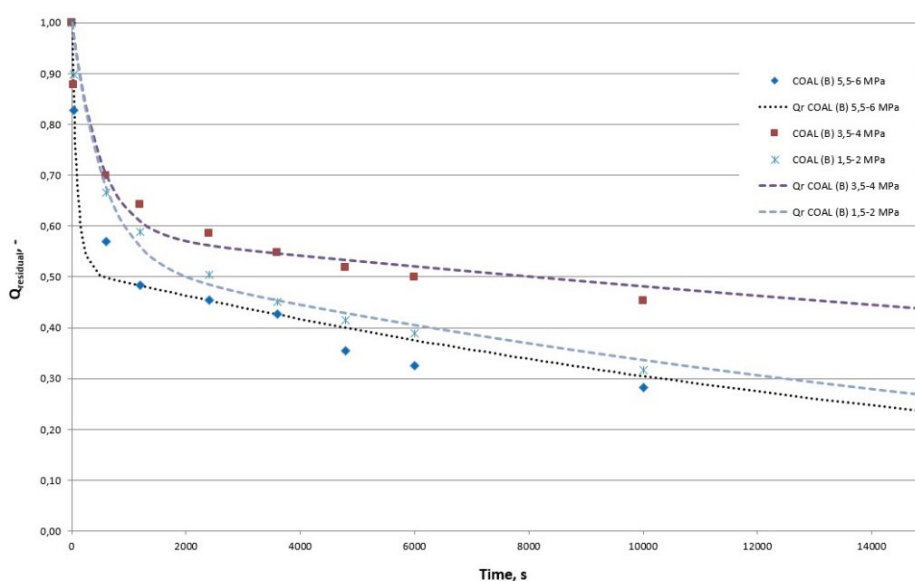**Figure 1.** Normalized CH_4 sorption equilibration rate at 5,5-6 MPa, 3.5-4 MPa and 1,5-2 MPa on coal A.

Figure 2. Normalized CH_4 sorption equilibration rate at 5,5-6 MPa, 3.5-4 MPa and 1,5-2 MPa on coal B.
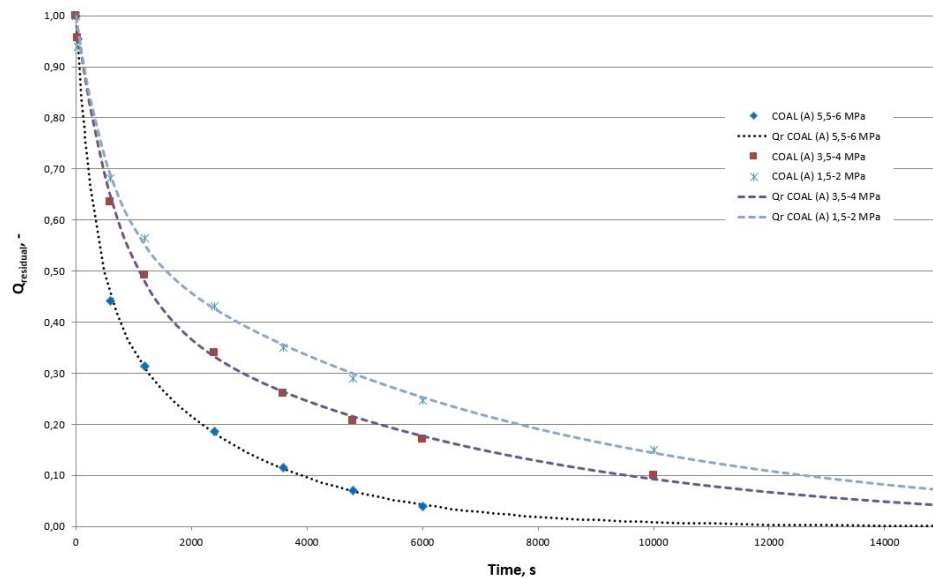
Figure 3. Normalized CO_2 sorption equilibration rate at 5,5-6 MPa, 3.5-4 MPa and 1,5-2 MPa on coal A.
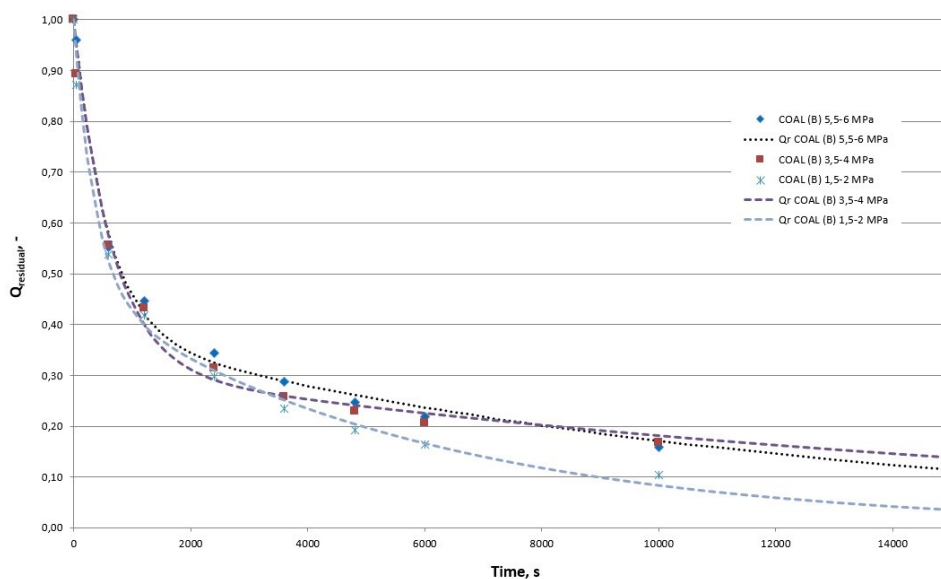

Figure 4. Normalized CO_2 sorption equilibration rate at 5,5-6 MPa, 3.5-4 MPa and 1,5-2 MPa on coal B.

When concerning coal B, results show that both fast and slow adsorption rates are faster at 5.5-6 MPa than at two other pressure ranges (except for CO_2). Hence, shortest diffusion time (4.6 days) for methane is at the highest pressure. This is not the case for CO_2 where diffusion times are considerably shorter.

Comparing the two types of coal, the 3.5-4 MPa pressure range accounts for the slowest diffusion time and quantity. Diffusion times are generally faster in coal B with also higher quantities of adsorbed gas in the fast adsorption rate. Coal A requires a longer diffusion process since this type of coal adsorbs more methane than coal B as shown in the previous study [3]. Experimental results show that diffusion rates are lower for CO_2 than for methane which is in agreement with other studies [5–7]. A slightly higher water content of coal B might have an impact on the diffusion time which was longer in case of CO_2.

The fraction of fast adsorption is considerably higher in CO_2 than in CH_4 by 15%-20% for the same pressure range and type of coal.

4. Diffusion rate and storage capacity

Laboratory experiments are not a direct representation of real CBM reservoir. The CBM reservoir is always filled with CH_4 and 100% recovery rates are rarely achievable. In case of ECBM process the CO_2 is injected into the reservoir saturated with CH_4. Aa result, the storage capacity varies in time, because the carbon storage capacity increases with time (injection) and a with desorption of methane. In fact longer time for CO_2 storage is required because the equilibrium will be reached when all the methane inside the coal will be desorbed.

This could be considered as a starting point for the application of simple management optimization models for the storage and production processes of CO_2 and CH_4. When analysing and comparing the diffusion functions of carbon dioxide and methane in coal at a certain pressure level it is possible to assess the storage and production processes and how they vary with the variation in pressure which is the only parameter than can readily be regulated.

In Table 3 a summary of the results obtained for the calculation of storage capacity in two cases: CO_2 is stored in empty reservoir (Case 1) and (Case 2) CO_2 is stored when methane is present inside the coal. These values show how different pressure levels correspond to different times of CO_2 storage and CH_4 production. The storage capacity variation in time has been calculated as the difference between the amount of CO_2 stored and the amount of CH_4 produced at a certain instant of time. Example of effective variation of the storage capacity at a certain pressure level in time in the first moments of the storage process are shown in Figure 5.

Table 3. Results of the storage capacity assessment in the function of time.

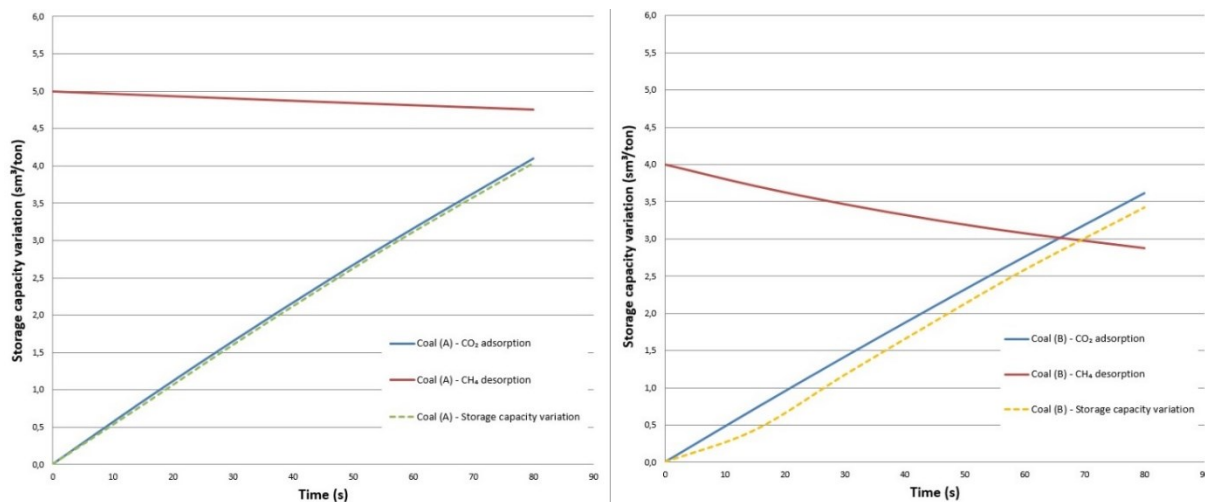| Coal A	5,5-6 MPa		3,5-4 MPa		1,5-2 MPa	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
CO_2 storage capacity (sm³/t)	30,97		27,96		22,68	
%variation from the max capacity	0%		-10%		-27%	
CH_4 production capacity (sm³/t)	5		5		5	
Time of Storage (s)	52000	607000	129000	1195000	149000	554000
Time of Storage (d)	0,6	7,0	1,5	13,8	1,7	6,4
%variation from the min storage time	10%		116%		0%	
Coal B	5,5-6 MPa		3,5-4 MPa		1,5-2 MPa	
	Case 1	Case 2	Case 1	Case 2	Case 1	Case 2
CO_2 storage capacity (sm³/t)	42,34		39,32		32,26	
%variation from the max capacity	0%		-7%		-24%	
CH_4 production capacity (sm³/t)	4		4		4	
Time of Storage (s)	252000	398000	373000	1065000	121000	447000
Time of Storage (d)	2,9	4,6	4,3	12,3	1,4	5,2
% variation from the min storage time	0%		120%		9%	

Figure 5. Graphical representation of CO storage, CH4 production and storage capacity variation trend in the first moments of the process in coal A and coal B at 5,5-6 MPa.

The selected diffusion model represents the adsorbed and desorbed quantities of gas in time as a fraction of the total capacity: cross-referencing those results with the values of the total storage capacity of CO_2 obtained through the storage capacity model, a quantification of the values becomes possible.

Concerning the production capacity of methane of the two coal samples, these values are site specific and their evaluation was not possible with the available equipment: therefore, an assumption on these values has been made based on the common values of similar coal types. It's important to notice that these values don't depend on the pressure of injection but on the characteristics of the reservoir; in these cases, the pressure of injection only rules the diffusion process and the time required to achieve the complete desorption of methane. From the Figure 5 it is evident that diffusion processes have an impact on the CO_2 injection time and CH_4 production.

5. Conclusions

The aim of this study was to verify the dynamic factor, that is the sorption rate which can directly affect the efficiency of CO_2 injection and as a consequence – storage. When aassessing the diffusion processes of CO_2 and CH_4 at different pressure levels, it was possible to understand how the CO_2 storage capacity of the coals varies in time due to the consequent desorption of methane which frees space for the storing of carbon dioxide. This phenomenon doesn't involve the creation of a higher storage capacity, but it shows how diffusion rate can have an impact on the injection time. The following conclusions can be drawn from this study:

- fast adsorption rate is higher at 5.5-6 MPa than at lower pressure range with highest fast adsorption rate fraction both for CH_4 and CO_2.
- lower (1.5-2 MPa) pressure range allows achieving sorption equilibrium in less time for both gases.
- diffusion rates are lower for CO_2 than for methane
- the CH_4 desorption rate has a slight impact on the CO_2 adsorption and as a consequence CO_2 storage capacity. The time to attain sorption equilibrium is in the range of a few hours.

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