



# Characteristics of carbon dioxide sorption in coal and gas shale – The effect of particle size



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## ABSTRACT

Gas retention mechanisms in shales are to some extent similar to that of coal. The gas is adsorbed in organic matter (mostly organic carbon) and clay minerals whereas transport of gas occurs in fractures. In the study two materials were analyzed— coal from the Upper Silesia Coal Basin and shale sample from Baltic Basin. The coal selected for experiments was a bituminous steam coal with 3.8%wt ash content. The shale sample was characterized by rather low TOC (1.1%) but high clay minerals content. The purpose of the study was to compare the high pressure CO<sub>2</sub> sorption characteristics of coal and gas shale and relate it to the particle size of samples subjected to tests. The size of the adsorbate has an impact on the sorption equilibrium time and reaching thermodynamic equilibrium occurs much faster in fine grained fractions. On the contrary, the particle size must reflect natural *in-situ* conditions and accessibility to the nano- and micropores where sorption occurs. In this study both sorbents were crushed and sieved into three particle size fractions and the CO<sub>2</sub> sorption was measured. The measurements were performed at the constant temperature of 55 °C and up to the pressure of 15–16 MPa. To model the sorption behavior a three parameter Langmuir model was fitted to experimental values. Results of the sorption tests show that the particle size of the sorbent has an impact on the obtained sorption isotherm. In case of coal, the difference in the sorption capacity could be related to the ash and inertinite content which are passing to fine particle size (<0.1 mm) whereas in shale it could be related to the area of exposed surface and extended time of sorption equilibrium.

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## 1. Introduction

Geological carbon dioxide storage as a part of Carbon and Capture Storage (CCS) technology has been the focus of extended research in the recent years. As potential natural traps of CO<sub>2</sub> - gas/oil reservoirs, coal seams and most commonly deep water/brine aquifers were identified. Although different trapping mechanisms govern the CO<sub>2</sub> storage in the above-mentioned reservoirs the basic idea is to inject CO<sub>2</sub> at high rates and permanently store it for thousands of years. The option to inject CO<sub>2</sub> into deep underground traps could be extended to shale gas reservoirs. In this case, CO<sub>2</sub> can be physically adsorbed on organic matter and/or clay minerals in the same way as methane. It is known from other research studies that CO<sub>2</sub> is preferentially adsorbed on the surface of organic matter in comparison to CH<sub>4</sub> – this is particularly apparent in case of coal (Busch et al., 2004; Ceglarska-Stefańska and Zarebska, 2005;

Battistutta et al., 2010; Pini et al., 2010; Busch and Gensterblum, 2011). Ceglarska-Stefańska and Zarebska (2005) conducted sorption tests on coals with moderate levels of metamorphism and the ratio of CO<sub>2</sub>/CH<sub>4</sub> sorption was approximately 3:1 (maximum pressure of experiment was 4.0 MPa). Busch and Gensterblum (2011) compared various sorption datasets of coals and it appears that CO<sub>2</sub> sorption is always higher than CH<sub>4</sub> but usually falls within the range of 2:1 and 3:1 ratio for dry coals. Apparently, the higher the degree of metamorphism of coal the lower the ratio since vitrinite-rich coals have much higher adsorption of CH<sub>4</sub> whereas the adsorption of CO<sub>2</sub> does not significantly increase for highly metamorphic coals like anthracite.

The mechanism of gas generation and storage in gas shales is somehow similar to that of coal (Table 1) therefore it is assumed that we can effectively store large volumes of CO<sub>2</sub> in organic rich shales. The study of Khosrokhavar et al. (2014) of manometric sorption of CO<sub>2</sub> and CH<sub>4</sub> on carboniferous shale from Belgium (organic matter content 6.6%) indicated the maximum ratio of CO<sub>2</sub>:CH<sub>4</sub> sorption was 3:1. In the experiments of Gasparik et al.,

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**Table 1**  
Comparison of gas generation, retention and flow mechanisms in gas shales and coals.

	Coalbed methane	Shale gas
Source	Coal acts as a source rock and as reservoir	Shale acts as a source rock and as reservoir
Trapping mechanism	Adsorption in coal matrix; diffusion into fractures; Darcy flow in fractures	Adsorption in matrix of organic matter, clay minerals; diffusive flow into fractures
Porosity	Low < 5–10%	Low < 5%
Permeability	0.5–80 mD 0.5–2 mD for European coals	0.0001–0.01 mD but significantly enhanced by hydraulic fracturing
Gas in adsorbed phase	90% of the total GIP	15–80% of the total GIP

2014 on Namurian (TOC 4.4%) and Posidonia (15.1%) shales the ratio of CO<sub>2</sub>:CH<sub>4</sub> sorption was also approximately 3:1.

In order to measure the volume of adsorbed gas in a function of pressure at constant temperature (sorption isotherm) it is necessary to select a representative sample from the reservoir (usually a core) and perform sorption experiments in the laboratory. There are two most common approaches to measure sorption on microporous adsorbents such as coals or gas shales i.e. gravimetric and manometric method. In gravimetric method a sensitive mass balance is used to measure changes in the sample weight as the sample is adsorbing gas (or other liquid) (Pini et al., 2006) whereas manometric method is based on the gas mass balance calculations. The principle of this method is explained later in this article as it was used to measure sorption in the analyzed samples.

In case of sorption measurements there are different intrinsic and extrinsic properties that may impact measured volume of gas adsorbed. Based on the literature of other authors (Sudibandriyo et al., 2003; Busch et al., 2009; van Hemert et al., 2009; Majewska et al., 2009; Busch and Gensterblum, 2011; Han et al., 2013; Gasparik et al., 2014; Vishal et al., 2015a, 2015b) some of the most important intrinsic and extrinsic factors that are related to the experimental measurements of gases on shales and coals have been selected. Major intrinsic properties of the sorbent are:

- Content of organic and mineral matter,
- Mineralogy of the rock – eg. type of clay minerals,
- Macerals content (in case of coals).

In case of the extrinsic properties we can distinguish basically three i.e.:

- Temperature of the sample under analysis,
- Moisture content of the sample,
- Particle size of the sample.

In fact, there are also other factors such as the accuracy of the setup, equations of state applied to calculate the density of the gas (or the compressibility factor) and the time at each step to attain sorption equilibrium that may also have a very profound impact on the measured sorption isotherm; particularly at high pressures. In some of the experiments the pressure drop related to the process of sorption is not properly controlled and may lead to insufficient time of sorption equilibrium. However, one of the most common problems associated with the sorption measurements on rock samples is the particle size of samples chosen for the experiments. In the vast majority of laboratory sorption experiments the rock samples are crushed and sieved to a given fraction (see Table 2) before the experiment starts. In this case, the smaller the particle size the faster the sorption process occurs and the sorption equilibrium time is shorter. Since in some of the cases (eg. CO<sub>2</sub> sorption on some coals) each step takes up to a few days, small particle size

significantly reduces the time needed to complete the experiments. On the other hand, the larger the sample the more representative it is for the reservoir conditions. In case of coals, crushing may lead to the breakage of natural fractures and matrix integrity whereas in case of gas shales it may cause some minerals to pass to the finest fractions and change the natural composition of the sample.

In this article, the impact of sample particle size of coal and shale on the sorption of CO<sub>2</sub> up to the pressures of 16 MPa is assessed. The experimental sorption results are compared with mineralogy of the shale and maceral content of coal in each fraction to validate the most appropriate sample size that would be recommended for sorption experiments.

## 2. Materials and methods

### 2.1. Materials

For the purpose of the study two materials were selected: Silurian gas shale (Lublin basin) from the approximate depth of 2643 m and bituminous coal from the Upper Silesian Coal Basin (Marcel Coal Mine). The coal selected for experiments is a typical steam coal (type 33 according to polish classification) with average ash content of 3.8%. The maceral composition of coal and ash content for each fraction is presented in Table 3. Chunks of coal acquired directly from the Run-of-mine conveyor were mixed in a large container. The volume of the large sample was reduced and homogenized by quartering to approximately 1 kg. For the purpose of experiments the coal was crushed in a jaw crusher, ball mill and sieved (dry sieving) into four fractions i.e. <0.1 mm (sample CA), 0.1–1.0 mm (sample CB), 2.0–10.0 mm (sample CC), >20 - (40) mm (sample CD). Coal samples were subjected to typical preparation procedure i.e. dried at 105 °C overnight and immediately after cooling in desiccator, weighted and placed in the sample cell. Hence, sorption was calculated on *Dry basis*.

The shale samples were prepared in a slightly different manner due to the limited availability of the material. An approximately 3 cm thick slice from a 100 mm diameter core was selected for the tests. Shale was crushed by hand, ground in a Netsch mortar grinder and sieved (dry sieving) into three fractions i.e. <0.1 mm (sample SA), 0.1–1.0 mm (sample SB), 1–2 mm (sample SC). The samples were weighted before placing in the sample cell of the sorption apparatus and left for 24 h on vacuum at 55 °C. It is believed that this procedure will not remove the clay-bond water and alter the shale structure (Gasparik et al., 2014). In any case, the samples were weighted again after the experiments in order to account for mass loss due to the water evaporation during vacuum drying and eliminate possible error in sorption calculation. Nevertheless, the sample used for the experiments should be considered as relatively dry - the moisture content was not exceeding 0.68%. The XRD quantitative analysis and TOC content of the averaged shale sample before the sorption test (*a priori*) is

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