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High-pressure sorption isotherms and sorption kinetics of CH_4 and CO_2 on coals

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ABSTRACT

Using a manometric experimental setup, high-pressure sorption measurements with CH_4 and CO_2 were performed on three Chinese coal samples of different rank ($VR_r = 0.53\%$, 1.20%, and 3.86%). The experiments were conducted at 35, 45, and 55 °C with pressures up to 25 MPa on the 0.354–1 mm particle fraction in the dry state. The objective of this study was to explore the accuracy and reproducibility of the manometric method in the pressure and temperature range relevant for potential coalbed methane (CBM) and CO_2-enhanced CBM (CO_2-ECBM) activities ($P > 8$ MPa, $T > 35$ °C). Maximum experimental errors were estimated using the Gauss error propagation theorem, and reproducibility tests of the high-pressure sorption measurements for CH_4 and CO_2 were performed. Further, the experimental data presented here was used to explicitly study the CO_2 sorption behaviour of Chinese coal samples in the elevated pressure range (up to 25 MPa) and the effects of temperature on supercritical CO_2 sorption isotherms.

The experiments provided characteristic excess sorption isotherms which, in the case of CO_2 exhibit a maximum around the critical pressure and then decline and level out towards a constant value. The results of these manometric tests are consistent with those of previous gravimetric sorption studies and corroborate a crossover of the 35, 45, and 55 °C CO_2 excess sorption isotherms in the high-pressure range. The measurement range could be extended, however, to significantly higher pressures. The excess sorption isotherms tend to converge, indicating that the temperature dependence of CO_2 excess sorption on coals at high-pressures (>20 MPa) becomes marginal. Further, all CO_2 high-pressure isotherms measured in this study were approximated by a three-parameter excess sorption function with special consideration of the density ratio of the "free" phase and the sorbed phase. This function provided a good representation of the experimental data.

The maximum excess sorption capacity of the three coal samples for methane ranged from 0.8 to 1.6 mmol/g (dry, ash-free) and increased from medium volatile bituminous to subbituminous to anthracite. The medium volatile bituminous coal also exhibited the lowest overall excess sorption capacity for CO_2. However, the subbituminous coal was found to have the highest CO_2 sorption capacity of the three samples. The mass fraction of adsorbed substance as a function of time recorded during the first pressure step was used to analyze the kinetics of CH_4 and CO_2 sorption on the coal samples. CO_2 sorption proceeds more rapidly than CH_4 sorption on the anthracite and the medium volatile bituminous coal. For the subbituminous coal, methane sorption is initially faster, but during the final stage of the measurement CO_2 sorption approaches the equilibrium value more rapidly than methane.

1. Introduction

China signed the Kyoto Protocol in May 1998, but as a developing country has no responsibility in reducing its greenhouse gas emissions so far. Looking at the long term, China, as the largest developing country and the largest CO_2 and coal mine methane emitter in the world, will have to reduce its greenhouse gas emissions sooner or later. In the mean time, China will still heavily depend on fossil fuels and continue to do so for decades to come. Therefore, technologies to reduce CO_2 emissions along with a continued use of fossil fuels are required at least for a transition period. Carbon dioxide capture and storage (CCS) in geological formations is considered as a promising short to intermediate term solution. One of the options considered here is the storage of CO_2 from large fossil fuel power plants in underground coal seams, and at the same time enhancing coalbed methane (CBM) recovery (CO_2-ECBM). CO_2-ECBM is envisaged to take advantage of the higher sorption capacity of the coal matrix for CO_2 as compared to CH_4. The conceptual approach postulates that CH_4 will be replaced by

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CO_2 by a preferential sorption process and mobilized to be produced more efficiently. This exchange will be controlled by the relative affinity of the two gases to the sorption sites (the thermodynamic component) and their relative mobility and sorption/desorption rates (the kinetic component). Many aspects of this concept are still speculative and only marginally supported by experimental or field data.

An improved understanding of the fundamental aspects of the interaction of CH_4 and CO_2 with the coal matrix under *in situ* gas pressure and temperature conditions is a prerequisite for the successful design and application of CO_2-ECBM and CO_2 coal seam sequestration and the appraisal of the technical feasibility. This involves the determination of accurate high-pressure sorption isotherms in the temperature ranges prevailing in deep coal seams. In recent years more and more high-pressure CO_2 and CH_4 sorption data have become available and some were recorded under realistic reservoir conditions ($P > 8$ MPa, $T > 35$ °C) [1–9]. However, the data quality still needs to be further refined. The accuracy of CO_2 sorption isotherms relies crucially on a precise assessment and control of the measuring temperature. This holds particularly for measurements conducted close to the critical temperature. Recent inter-laboratory studies have clearly revealed problems in terms of reliability and comparability of sorption data [10,11]. The objective of the present study was to improve the quality of the manometric measuring technique for high-pressure CH_4 and CO_2 sorption on coal samples and to identify and eliminate potential pitfalls. The focus was on the establishment of essentially identical measuring conditions, precise control of all relevant parameters, and the assessment of reproducibility and consistency of the results. Furthermore, sorption measurements on the three Chinese coal samples presented here were focused explicitly on the elevated pressure region (4–25 MPa), and the influence of temperature on supercritical CO_2 isotherms was investigated intensively.

In this study experiments were performed on three representative coal samples of different rank from different Chinese coal basins. Sorption experiments were carried out at 35, 45, and 55 °C on dry coals and pressures up to 25 MPa (250 bar). The general goal was to contribute to an improved understanding of the physical interactions of methane and CO_2 with coals at elevated pressures and temperatures corresponding to those typically encountered in CBM/ECBM operations. Experimental results on equilibrium sorption capacities of CO_2 and CH_4 and the kinetics of the sorption process provide a database for reservoir simulations in CO_2-ECBM exploitation.

2. Samples

The aim of this study, was to investigate fundamental aspects of the interaction of methane and carbon dioxide with coals. The samples were selected such as to cover a large maturity range and a significant variability in composition. They comprise one Jurassic coal of subbituminous rank and two Permo-Carboniferous coals of medium volatile bituminous and anthracite rank from three different Chinese coal basins. The samples were obtained directly from the working faces by local coal mine companies of Inner Mongolia (Baorixile, Hulun Buir), Shanxi (Wangtaipu, Jincheng), and Henan (Bakuang, Pingdingshan) provinces. The locations of these coal mines are shown in Fig. 1. Related geological information has been compiled in several previous publications [12–18]. From these samples, representative aliquots were selected and prepared as reported below. Coal sample properties and origins are listed in Table 1. The random vitrinite reflectance values (VR_r) of the coal samples are 0.53%, 1.20%, and 3.84%, respectively with vitrinite contents ranging from 24.6% to 85.4%. Ash yields differ significantly and vary from 11% to 22.6%. Total organic carbon contents (TOC) range from 76.9% to 84.9% for the three coals.

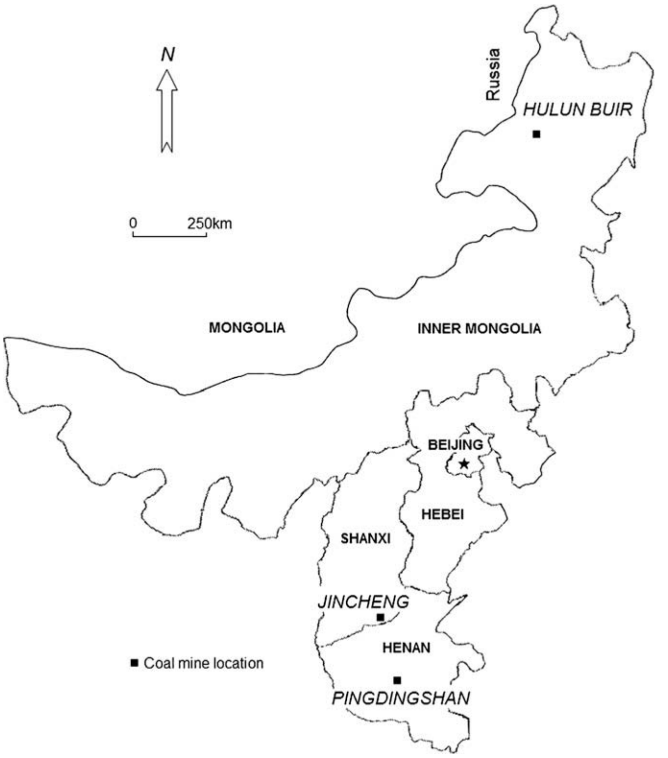

Fig. 1. Locations of Chinese coal mines from which samples used in this study were taken.

3. Methods

3.1. Sample preparation

The coal samples were crushed and ground to pass through a 1 mm sieve. The <0.354 mm particle fraction (amounting to <5% of the total sample) was discarded and the 0.354–1 mm fraction was used for all measurements. The main purpose of this cut-off was to avoid fines passing the in-line 2 μm filter and entering the high-precision valves. As shown by Busch et al. [19] this procedure may result in some degree of fractionation and distortion of maceral composition and ash yield as compared to the bulk coal sample. Considering the small amount of discarded material this potential fractionation effect is, however, considered negligible.

Moisture contents of the as received (a.r.) coal samples were determined according to the German standard method (DIN 51718) by heating to 105 °C for >90 min under vacuum. Moisture and ash yield were subsequently used for normalization of the sorption data to the dry, ash-free (d.a.f.) basis. All measurements were performed using the dry coal samples. Samples were transferred immediately to the sample cell to prevent oxidation and/or hygroscopic moisture uptake after drying.

3.2. Sorption experiments

Excess sorption isotherms were measured using the manometric method as described by Krooss et al. [1] and Busch et al. [20]. Powdered coal samples were placed into a calibrated sample cell ($9.223\ cm^3$) equipped with an in-line filter with 2 μm pore size. Both, reference cell and sample cell were kept in a temperature-controlled oven.