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Coal lithotypes before and after saturation with CO_2; insights from micro- and mesoporosity, fluidity, and functional group distribution

M. Mastalerz [a,*], A. Drobniak [a], R. Walker [b], D. Morse [c]

[a] *Indiana Geological Survey, Indiana University, 611 North Walnut Grove Ave., Bloomington, IN 47405-2208, USA*
[b] *Pearson Coal Petrography, 7300 W. 15th Ave, Gary, IN 46406, USA*
[c] *Illinois State Geological Survey, University of Illinois, Champaign, Illinois, 61820, USA*

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ABSTRACT

Four lithotypes, vitrain, bright clarain, clarain, and fusain, were hand-picked from the core of the Pennsylvanian Springfield Coal Member (Petersburg Formation) in Illinois. These lithotypes were analyzed petrographically and for meso- and micropore characteristics, functional group distribution using FTIR techniques, and fluidity. High-pressure CO_2 adsorption isotherm analyses of these lithotypes were performed and, subsequently, all samples were reanalyzed in order to investigate the effects of CO_2. After the high-pressure adsorption isotherm analysis was conducted and the samples were reanalyzed, there was a decrease in BET surface area for vitrain from 31.5 m^2/g in the original sample to 28.5 m^2/g, as determined by low-pressure nitrogen adsorption. Bright clarain and clarain recorded a minimal decrease in BET surface area, whereas for fusain there was an increase from 6.6 m^2/g to 7.9 m^2/g. Using low-pressure CO_2 adsorption techniques, a small decrease in the quantity of the adsorbed CO_2 is recorded for vitrain and bright clarain, no difference is observed for clarain, and there is an increase in the quantity of the adsorbed CO_2 for fusain. Comparison of the FTIR spectra before and after CO_2 injection for all lithotypes showed no differences with respect to functional group distribution, testifying against chemical nature of CO_2 adsorption. Gieseler plastometry shows that: 1) softening temperature is higher for the post-CO_2 sample (389.5 °C vs. 386 °C); 2) solidification temperature is lower for the post-CO_2 sample (443.5 °C vs. 451 °C); and 3) the maximum fluidity is significantly lower for the post-CO_2 sample (4 ddpm vs. 14 ddpm).

1. Introduction

Concerns about increasing concentrations of CO_2 in the atmosphere have resulted in numerous investigations towards reduction of carbon dioxide emissions from point sources (coal-fired power plants, natural-gas-burning sources). Storage of CO_2 in deep coal beds is one option being considered to reduce CO_2 emissions. Many laboratory studies of CO_2 adsorption into coal have been conducted over the last several years (e.g., Ceglarska-Stefanska and Czaplicki, 1993; Clarkson and Bustin, 1999; Krooss et al., 2002; Mazumder et al., 2006; Cui et al., 2007; Bustin et al., 2008) providing information about rates and volumes of adsorbed CO_2, as well as selectivity of CO_2 over methane. These and several other studies have provided a basis for discussion about gas adsorption mechanisms in coal (Milewska-Duda et al., 2000; Goodman et al., 2005; Mazumder et al., 2006) and the changes in the structure of the coal resulting from the adsorption of CO_2 (Larsen, 2004). However, in spite of the great number of studies on CO_2 adsorption in the coal, important questions about the mechanisms of CO_2 sorption in coal and the effects of the sorption on the coal matrix remain unanswered.

Understanding carbon dioxide interactions with coal is important both to model gas injectivity changes over time and to predict long-term effects of CO_2 storage on the coal and surrounding rocks. However, the influence of injected CO_2 on coal structure is not well understood. Studies show that upon initial contact of injected fluids with the coal, there is very fast adsorption of the fluid on the coal surface, and that this is followed by slow diffusion into the coal (Hsieh and Duda, 1987). This process of diffusion (and dissolution of fluid in the coal) is commonly explained by the principles of polymer chemistry and the transformation of initially glassy, brittle, cross-linked macromolecules of coal into rubbery, viscous, still cross-linked macromolecules, where CO_2 lowers this “glass to rubber” transition temperature (Khan and Jenkins, 1985; Larsen et al., 1997; Larsen, 2004; Karacan, 2007). In such an interpretation, CO_2 acts as a plasticizer, as documented earlier for polymers (Wang et al., 1982).

One of the unresolved questions is whether CO_2 sorption is solely a physical phenomenon or if there is also a chemical reaction of CO_2 with functional groups of coal's organic matter. Arguments exist for both possibilities. For example, based on high-pressure static and dynamic experiments on coal, Mazumder et al. (2006) conclude that “chemical

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* Corresponding author.
E-mail address: mmastale@indiana.edu (M. Mastalerz).

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reactions involving CO_2 cannot be ruled out," although no direct evidence has been demonstrated in that study. Kolak and Burruss (2006) found that during CO_2 injection process some polycyclic aromatic hydrocarbons were liberated and mobilized in the coal, suggesting that chemical interactions take place. Results of other studies suggest that there are no interactions between injected CO_2 and coal functional groups (e.g., Goodman et al., 2005), pointing to the physical process of adsorption. Regardless of the physical or chemical nature of CO_2 sorption, it has been widely documented that CO_2 injection at high pressure results in swelling of the coal matrix (Reucroft and Patel, 1986; Ceglarska-Stefanska and Czaplicki, 1993) and that the amount of swelling depends both on coal rank and coal type (e.g., Gentzis et al., 1996; Astashov et al., 2008; Balan and Gumrah, 2009).

The main objective of this paper is to compare the characteristics of coal lithotypes (distinct lithological units of coal) before and after CO_2 injection at high pressure to investigate chemical and physical effects and responses on each coal lithotype. To address this issue, petrographic analysis, mesopore and micropore characteristics, functional group distribution, and plasticity and fluidity of coal were compared before and after CO_2 injection.

2. Methods

Four lithotypes, vitrain, bright clarain, clarain, and fusain, were hand-picked from a core of the Pennsylvanian Springfield Coal Member (Petersburg Formation) from the Tanquary CO_2 injection site in Illinois (Morse et al., in review). It is high volatile bituminous coal with vitrinite reflectance (R_o) of 0.63%. Maceral composition of these lithotypes is presented in Table 1 and demonstrates a progressive decrease in vitrinite and an increase in inertinite from vitrain to fusain.

High-pressure CO_2 adsorption isotherm analyses were performed on samples of all lithotypes crushed to 60-mesh size, using a high-pressure volumetric adsorption instrument. All isotherm were run on moisture-equilibrated samples at 20 °C, corresponding to the coal reservoir temperature. The analysis and data collection followed the procedure outlined in Mavor et al. (1990) and the adsorption isotherms are shown in Fig. 1. Lithotypes before and after high-pressure CO_2 adsorption isotherm runs were analyzed for meso- and micropore characteristics utilizing low-pressure gas adsorption, functional group distribution using FTIR techniques, and fluidity using a Gieseler platometer. Analyses on original lithotype samples, except Gieseler plastometry, were conducted a few of days after sampling. Splits of these lithotypes after high pressure isotherm analysis were analyzed about three months later, immediately after high pressure isotherm analyses had been completed. For Gieseler plastometry, the original bright clarain sample and its split after high pressure isotherm analyses were run the same day. From the moment of sample collection to the time of analyses, the samples were kept in an environmental chamber to prevent oxidation.

2.1. Micro- and mesoporosimetry

Low-pressure gas adsorption measurements were conducted on a Micromeritics ASAP-2020 apparatus (Mastalerz et al., 2008b). Coal samples weighing 1 to 2 g were analyzed both with nitrogen and carbon dioxide gases to obtain information about the mesopore (2–50 nm, accessible to both gases) and micropore structures (<2 nm, accessible only to carbon dioxide). Before analysis with either N_2 or CO_2, the samples were automatically degassed by heating at ~110 °C in a vacuum for about 14 h to remove adsorbed moisture and volatile matter. For quantifying nitrogen gas adsorption, the temperature of the sample is reduced to the temperature of liquid nitrogen. For CO_2 adsorption, the temperature of the sample is 0 °C. The instrument's computer software automatically generates adsorption isotherms and calculates surface areas, pore volumes, and pore distributions based on multiple adsorption theories, i.e., Langmuir, Brunauer–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH), Dubinin–Radushkevich (D–R), and Dubinin–Astakhov (D–A), among others (Clarkson and Bustin, 1999; Webb and Orr, 1997). A detailed description of these theories and techniques can be found in Gregg and Sing (1982).

2.2. Fourier Transform Infrared Spectrometry (FTIR)

Samples for FTIR investigation were prepared by the potassium bromide (KBr) pellet method using a small amount (approximately 2 wt.% of the mixture) of the coal material mixed with finely ground KBr. A Nicolet 6700 FTIR spectrometer with DTGS detector was used; the resolution was 4 cm^{-1}, and 300 scans per sample were recorded in the 400 and 4000 cm^{-1} wavenumber region.

2.3. Gieseler fluidity

Gieseler fluidity was measured by the use of a constant torque plastometer, wherein a constant torque was applied to a stirrer placed into a crucible into which the coal sample was charged. The crucible was then placed into a lead solder bath and the temperature raised at a constant 3° per minute from 325 °C to 540 °C. The rate of stirrer motion was recorded in relation to the temperature, giving a relative measure of the plastic behavior of coal in dial divisions per minute (ddpm). Air-dried coal samples were crushed to 40-mesh size (0.42 mm), and 5 g loaded into the sample crucible as per ASTM D2639-98 (ASTM, 2008).

3. Results

Petrographically, there is no difference between original lithotypes and lithotypes that experienced high pressure CO_2. Vitrain, a lithotype that is expected to be most reactive among all lithotypes studied (Mastalerz et al., 2008a), does not show any evidence of plasticization of vitrinite fragments (e.g., rounding of edges) (Fig. 2A, B). Liptinite macerals, sporinite and cutinite, do not show any change in their preservation (Fig. 2C, D) or fluorescent properties. There is a difference in vitrinite reflectance from 0.60% in the original vitrain sample to 0.59% in the vitrain sample after exposure to high pressure CO_2 (Fig. 2E, F). This is minimal difference that can easily result from differences within the original material.

3.1. Comparison of meso- and microporosity of lithotypes before and after CO_2 adsorption

Fig. 3A shows low-pressure nitrogen adsorption isotherms for vitrain, bright clarain, clarain, and fusain before and after high-pressure CO_2 adsorption. Among four lithotypes, vitrain shows the most distinct

Table 1
Petrographic composition (in vol. %) of the lithotypes studied. Telovit. — telovitrinite, Detrovit. — detrovitrinite, Gelovit. — gelovitrinite, TV — total vitrinite, Spor. — sporinite, Cut. — cutinite, TL — total liptinite, Semifus. — semifusinite, Fus. — fusinite, Inertodet. — inertodetrinite, TI — total inertinite, MM — mineral matter.

Lithotype	Telovit.	Detrovit.	Gelovit.	TV	Spor.	Cut.	TL	Semifus.	Fus.	Inertodet.	TI	MM
Vitrain	89.6	4.2	0.0	93.8	1.2	0.6	1.8	1.0	0.0	1.8	2.8	1.6
Bright clarain	63.8	8.2	0.0	72.0	4.2	0.0	4.2	2.6	6.2	7.8	16.6	7.2
Clarain	50.6	14.0	0.0	64.6	4.6	0.0	4.6	11.0	6.2	8.0	25.2	5.6
Fusain	4.6	0.8	0.0	5.4	1.0	0.0	1.0	6.2	81.2	6.2	93.6	0.0