Role of pH on CO_2 sequestration in coal seams

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ABSTRACT

The effect of acidic or basic pre-treatment on the adsorption capacity of CO_2 on coals was investigated. Argonne Premium Pocahontas No. 3, Upper Freeport, Pittsburgh No. 8, Lewiston–Stockton, Blind Canyon, Illinois No. 6, Wyodak, and Beulah–Zap coals were washed in weak solutions of H_2SO_4 and NaOH to the pH values of 10, 7, and 2, after an initial washing in acidic water. Attempts to treat the Wyodak and Beulah–Zap coals were unsuccessful because the base treatment after the initial acid treatment resulted in a suspension which could be separated neither *via* filtration through a 45 μm filter nor centrifugation. Equilibration took several days in some cases, although the as-received coal had been ground to 150 μm. Acid washing preferentially removed Ca (calcite) and Mg. Aluminosilicate clays were not notably removed. Iron was removed in significant amounts only after base treatment, possibly after it was converted to hematite. The adsorption capacity of CO_2 on the acid treated coals was higher than both the base treated and untreated coals. The difference in adsorption capacities for acid and base treated coals was related to the pore sizes and mineral matter removal from the coals, where the calculated average pore size was higher for acid treated coals than for the base treated coals. It is concluded that the pH decrease due to CO_2 dissolution in cleat water is favored in coal seam sequestration, which resulted in an increase in storage capacity of coals.

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1. Introduction

Sequestration of carbon dioxide (CO_2) in unmineable coal seams is one of the geological strategies being considered to mitigate increasing atmospheric concentrations of CO_2 [1,2]. Injected CO_2 is expected to flow through the natural fractures within the coal seam and to diffuse into and be sorbed by the organic matrix of the coal [3–8]. It is also expected that the injected CO_2 will lower the pH of any water entrained in, or wetting the surface of, the coal due to the high-pressure dissolution of CO_2 [1,9–11]. In addition, some sequestration scenarios include co-sequestration of the acidic gases such as SO_x and NO_x, which would depress the pH further [10,12]. Post-sequestration scenarios may also include the intrusions of fresh water or brines long after the sequestration field has been abandoned, which could lead to alterations in the pH [13]. It is recognized that the adsorption capacities of coals are dependent on a number of factors including temperature, pressure, rank and moisture content of coals [1,2,14,15]. However, the effect of the pH of the surrounding media on the adsorption capacity of the coal matrix and the stability of the adsorbed CO_2 has not been extensively studied.

Change in pH can affect the coal and CO_2 sequestration in several ways. A decrease in pH can dissolve and extract mineral matter associated with the coal [16,17]. A pH change can alter the surface charge of the coal [18] and disturb the intermolecular interactions including hydrogen bounding, van der Waals interaction, electrostatic forces, and ionic interactions responsible for the 3-dimentional (3-D) structure of the macromolecular network [19–21]. Because the aperture size of a pore in the coal is important for gases to access within the pores and because the maximum adsorbed amount is related to the pore volume [22], all of these may affect the storage capacity of the coal and the stability of the adsorbed CO_2.

Injected CO_2 into a coal seam will decrease the pH and dissolve and extract the mineral matter. Mineral matter in coal takes two forms: inherent mineral matter and extraneous mineral matter. Inherent mineral matter is found in relatively minor amounts in the coal [23]. These minerals, once present as nutrients in the original plant matter, were trapped in microscopic amounts during the coalification process and, as a result, have become part of the organic matrix [24]. The inherent mineral matter is generally found embedded within the micropore system of the coal, associated with the organic matrix, and cannot be easily removed [25]. The second type of mineral matter is referred to as extraneous mineral matter. These minerals have entered the seam via aqueous seepage

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during the coalification process. Because they tend to fill larger cleats and fissures, extraneous deposits can range in size from a few hundred microns to several cubic feet [26]. The bulk of extraneous mineral matter is composed mainly of pyrite, calcite, quartz, and aluminosilicate clays [26]. With the possible exception of quartz, these minerals are affected by either acidic or basic surroundings through dissolution or ion-exchange. Calcite is particularly sensitive to acidic aqueous surroundings [17].

In addition to the extraction of mineral matter, changes in pH can alter the overall surface charge of coals [18]. It is well recognized that solids in contact with solutions with a pH above their isoelectric point acquire a net negative surface charge; those in contact with solutions with a pH below their isoelectric point acquire a net positive surface charge. The isoelectric point was reported to be about pH $\sim$ 3.8 for coals [18]. The CO_2 sequestration in water saturated coal seam will certainly decrease the pH in the sequestration environment, the degree to which is dependent of the pressure of the CO_2. Thus, the acidic pH would replace the carboxylic salts, such as $R-CO_2M^{+1}$ and $(R-CO_2)_2M^{+2}$ with the $R-CO_2H$ form [27]. Similarly, less reactive, and less common, phenolic groups in the coal matrix would be affected, transforming $Ar-O-M^{+2}$ to $Ar-O-H$. Here, $Ar-$ represents the aromatic rings. Ubiquitous nitrogen-containing groups, which are almost always found in heterocyclic forms, usually take the form of basic pyridine groups in higher-rank coals, and acidic pyrrole derivatives in lower ranks [28]. Sulfur also plays a role in the organic matrix; however, most of it is in the form of $-SH$ groups [26]. Nitrogen and organic sulfur groups typically do not interact with mineral matter in coal and therefore can not be removed by acid or base treatment although their chemical attributes can be changed. Consequently, the properties of surface of a coal may change due to inherent surface charge and the chemical composition of coal.

Change in surface charge may disrupt the intermolecular interactions responsible for the 3-D structure of the macromolecular network. The 3-D structure of coal is mainly maintained by the covalent bonding as well as the secondary forces, the most important of which are hydrogen bounding, van der Waals interaction, electrostatic forces, and ionic interactions [29,30]. Disturbances in such interactions may destroy the 3-D structure of coals, which may affect the swelling and shrinkage properties as well as the porous structure of the coal.

Any changes in pH during the CO_2 injection may enhance the CO_2 storage. Literature is limited to clearly indicate the effect of pH on the adsorption capacity and stability of the adsorbed CO_2 on coals. For instance, Larsen et al. [21] showed that demineralization did not affect the macromolecular structure of coals apart from those due to ion exchange and removal of inorganics. Mahajan and Walker [31] found random and significant changes in surface areas of coals measured by adsorption of N_2 and CO_2 after removal of the inorganic matter from the coal by acid treatment. Changes in surface areas of raw coals were attributed to both physical removal of inorganic matter from the aperture cavity system and the adsorption of acid on the coal surface. Nishino [32] showed that CO_2 adsorption on demineralized coal increases proportionally to the concentration of carboxylic groups present on the coal's surface. Goodman et al. [33,34] have shown that CO_2 did not interact with the adsorbed water in coal evidenced by Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR). Nevertheless, studies of the effects of acidic and basic solutions on coal have frequently focused on the demineralization of the coals [17,19,21,31]. Most of these investigations have involved leaching the mineral matter in coal with concentrated acid and base solutions at elevated temperatures [21,31]. Results gathered from these studies are of questionable applicability to carbon sequestration science because the coals have been exposed to more extreme acidic or basic concentrations

than they would be in a natural sequestration setting. Additional studies which attempt to simulate environmental levels of acid and base is needed to better reflect the chemistry under *in situ* conditions.

The current study attempts to investigate the effects of weak acidic and basic conditions on the coal seam sequestration of CO_2. For this purpose, the various ranks of Argonne Premium coals were treated in acidic, neutral, and basic pH conditions using dilute H_2SO_4 and NaOH solutions. In order to eliminate or reduce the influence of the mineral matter removal during the subsequent pH treatments, each coal was subjected to an initial acid treatment. Thus, with further pH treatment, it was attempted to adjust the surface charge of the coals to acidic, neutral, and basic pH values in order to compare the adsorption capacity of CO_2 on these treated coals.

2. Experimental

2.1. Coal samples and solutions

Coals were obtained from the Argonne National Laboratory through the Premium Coal Sample Program [35]. The proximate and ultimate analyses of the Argonne coals used are shown in Table 1 [35]. The coal samples were received in glass ampoules pulverized to a -100 mesh or less than 150 μm of particle size. The sample handling was performed in an inert gas (helium) flushed glove bag under a positive pressure of He. Because coals rapidly and irreversibly adsorb atmospheric oxygen [36], efforts were devoted to maintain an oxygen-free environment. Vials of the Argonne Premium coals were opened after they were well-mixed in accordance with the provided mixing instructions [35]. Coal samples were removed from the glove bag only after they had been placed in the sample cell and capped.

Two acid solutions, one dilute and the other more concentrated, were prepared by diluting 1.0 and 5.0 ml portions of $\sim$36 N H_2SO_4 with 125 ml apiece of de-ionized, de-aerated water. Similarly, two NaOH solutions, one dilute and the other more concentrated, were prepared by diluting 1.0 and 5.0 ml portions of 50 wt% NaOH solution with 125 ml de-ionized water. In any case, these dilute and more concentrated acid (H_2SO_4) and base (NaOH) solutions are no more than 3 and 15 wt%, and 0.4 and 2 wt%, respectively.

2.2. pH treatment of coal samples

A diagram of the sample preparation procedure is shown in Fig. 1.

2.2.1. Initial acid treatment
Each coal sample was placed into 100 ml of de-ionized water (resistivity 18.2 MΩ) in a 500 ml beaker and magnetically stirred to form an aqueous slurry. The slurry was then titrated to an equilibrium pH range of 1.90–2.10 with H_2SO_4 solution delivered in 1.0-ml increments with an auto pipette at room temperature. The more concentrated acid was used initially then the more dilute as the desired end point was approached. The pH was measured frequently using an Orion Ross Ag/AgCl electrode, and the final two readings were normally several hours apart to ensure complete equilibration. The acid-washed coal was vacuum filtered, using sterile 45 μm cellulose nitrate filters. The filtrate was saved for later analysis. The entire process was performed under a N_2 atmosphere in a glove bag.

2.2.2. Base treatment
In the glove bag under a N_2 atmosphere, the acid-treated coal was transferred to a clean 500 ml beaker, where it was again slurried with 100 ml of de-ionized water. The slurry was then titrated

Table 1
Proximate and ultimate analyses of the Argonne Premium coal samples [57].

| Coal sample		Proximate analysis (wt%)				Ultimate analysis (wt%, daf)				
Seam	State	Rank	Moisture	Ash[a]	VM[a]	C	H	O	S	N
Pocahontas No. 3	VA	Low Vol. Bit.	0.65	4.74	18.48	91.05	4.44	2.47	0.50	1.33
Upper Freeport	PA	Med. Vol. Bit.	1.13	13.03	27.14	85.50	4.70	7.51	0.74	1.55
Pittsburgh No. 8	PA	High Vol. Bit.	1.65	9.10	37.20	83.20	5.32	8.83	0.89	1.64
Lewiston–Stockton	WV	High Vol. Bit.	2.42	19.36	29.44	82.58	5.25	9.83	0.65	1.56
Blind Canyon	UT	High Vol. Bit.	4.63	4.49	43.72	80.69	5.76	11.58	0.37	1.57
Illinois No. 6	IL	High Vol. Bit.	7.97	14.25	36.86	77.67	5.00	13.51	2.38	1.37
Wyodak-Anderson	WY	Subbit.	28.09	6.31	32.17	75.01	5.35	18.02	0.47	1.12
Beulah–Zap	ND	Lignite	32.24	6.59	30.45	72.94	4.83	20.34	0.70	1.15

[a] Dry basis.
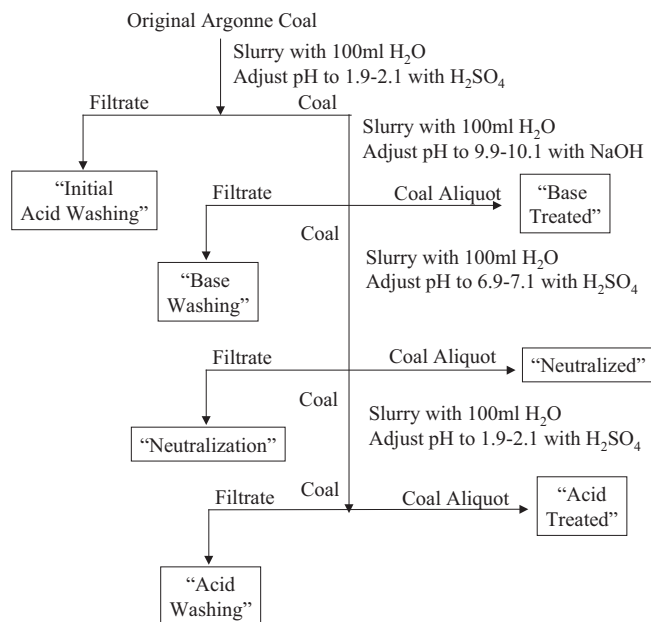
Fig. 1. Schematic showing the preparation of the coal samples.

to an equilibrium pH range of 9.90–10.10 with NaOH solutions delivered in 1.0 ml increments with an auto pipette at room temperature. The more concentrated base was used initially, then the more dilute as the desired end point was approached. Slow reaction times, especially for the lower-rank coals, often necessitated several days to achieve complete equilibration. The filtrate was saved for later analysis. The coal was vacuum filtered, and allowed to dry under inert gas atmosphere for several hours and approximately one-third of the coal was reserved for measurements as the "Base-Treated" coal.

2.2.3. Neutralization

The remainder of the base-treated coal was slurried with 100 ml of de-ionized water in a clean 500 ml beaker in the glove bag under a N_2 atmosphere. The slurry was neutralized by titrating with the acid solutions to attain an equilibrium pH in the range of 6.90–7.10. Because the previous washings had removed much of the buffering capacity, back titrations with NaOH were sometimes necessary to achieve equilibrium in this pH range. The lower buffering capacity also resulted in a faster equilibration time. After treatment, the coal was vacuum filtered and allowed to partially dry. The filtrate was saved for later analysis. Approximately half of the coal samples were reserved as the "Neutralized" coal sample.

2.2.4. Final acid treatment

The remaining coal sample was slurried with 100 ml of de-ionized water in a clean 500 ml beaker in the glove bag under a

N_2 atmosphere. The slurry was then titrated to an equilibrium pH in the range of 1.90–2.10 with H_2SO_4 solutions delivered in 1.0-ml increments with an auto pipette at room temperature. The coal was vacuum filtered, and allowed to dry under the inert gas atmosphere for several hours. The filtrate was saved for later analysis. The coal sample was then reserved for measurements as the "Acid-Treated" coal.

Finally, all of the treated coal samples were placed in a vacuum oven contained within a glove bag for an oxygen-free environment and dried. The coals were dried at 75 °C repeatedly for four-hour periods until a constant weight (+/− 1%) was obtained for two subsequent weightings.

2.3. Estimation of ash content and metal analysis of washing extracts

The ash contents of the coal samples were obtained according to ASTM D 2795-95 – Standard Test Method for Analysis of Coal and Coke Ash. Metal analysis of the extracts was performed using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

2.4. Adsorption isotherm measurements

The adsorption isotherms of CO_2 on the pH treated and non-treated Argonne Premium coal samples were obtained by volumetric method. A description of the high-pressure manometric gas adsorption apparatus and isotherm measurement method can be found elsewhere [11,15,37,38]. Briefly, the apparatus consisted of a reservoir cell of approximately 13 ml and a sample cell of about 6 ml; both submerged within a temperature-controlled water bath (±0.1 °C). The pressure transducers for each sample cell were calibrated in the pressure range studied. Cell volumes were estimated by the He-expansion method. An ISCO syringe pump was used to deliver pressurized He or CO_2 with a purity of 99.997% and 99.999%, respectively. A pressure range of 0–4 MPa was used at 22 °C. A 0.6–1.3 g aliquot of coal was used in each experiment. Each sample was dried in-situ at 80 °C under vacuum for 36 h before any measurements were performed. The void volume of each sample cell, V_o, was estimated by helium expansion method prior to the measurement of the adsorption isotherms.

After removing the helium under vacuum, the reservoir cell was pressurized with CO_2. About 10 min were allowed to achieve thermal equilibrium, although a stable temperature reading was achieved in about 3 min. Then, a portion of the gas was transferred from the reference cell into the sample cell. Pressure and temperature were monitored in both cells to verify thermal and adsorption equilibrium. A 20–30 min of equilibration time was sufficient for the adsorption of CO_2 on powdered coal samples (150 μm or −100 mesh) to reach equilibrium. The amount of CO_2 within both the reference and sample cell were calculated using the real gas law, which accounts for the gas compressibility [39]. From the mass balance, the difference between the moles of CO_2

transferred from the reservoir cell, n^t, and the moles of CO_2 calculated to be present in the He-estimated free-gas phase in the sample cell, V_o, was considered to be the Gibbs excess adsorption, Δn^{ex}. The reference cell was then pressurized with additional CO_2 and the process was repeated. Adsorption isotherms were plotted as the total amount of excess adsorbed CO_2, n^{ex}, versus the measured equilibrium pressure.

2.5. Evaluation of the adsorption isotherm data

The CO_2 adsorption isotherm data were modeled using modified Dubinin–Astakhov equation, Eq. (1) [11,37,38], assuming a pore filling mechanism

$$n^{ex} = (1 - \rho/\rho^a)n_o e^{-\left[\frac{RT}{\beta E_o}\ln(P_S/P)\right]^j} + \rho\Delta V \quad (1)$$

where n^{ex} is the experimentally measured amount of adsorption, ρ is the density of the gas phase, ρ^a is the density of the adsorbed phase, n_o is the adsorption/micropore capacity, β is the affinity coefficient between CO_2 and the coal (β = 0.35 for CO_2) [40], E_o is the characteristic heat of adsorption, j is the structural heterogeneity parameter, P_s is the saturation pressure, R is the universal gas constant, T is the temperature, and ΔV is the unaccounted-for volume due to the gas solubility in the coal matrix, to the coal swelling, and to any over- or under-estimation of the void volume (V_o) in the sample cell due to the assumptions underlying the choice of helium as the reference gas in the adsorption experiments [41–46]. The saturation pressure (P_s) and the density of the adsorbed phase (ρ^a) were calculated using the relationships suggested by Reid et al. [47] and Dubinin [48], respectively. The calculated values were P_s = 5.886 MPa and ρ^a = 3.866 mmole/cm³ at 22 °C. Curve fitting was performed using the *SigmaPlot®* spreadsheet regression data analysis.

When Eq. (1) is fit to the excess adsorption isotherm data, the parameters, such as the adsorption capacity (n_o), the characteristic heat of adsorption (E_o), the Dubinin coefficient (j), and the volumetric changes (ΔV) can be obtained from the best fit solution of the CO_2 excess adsorption isotherm data. The surface area, isosteric heat of adsorption, and the average pore size of coals can also be calculated using these parameters.

2.5.1. Calculation of surface area of coals
The surface areas of coals is calculated from the CO_2 adsorption capacity using Eq. (2):

$$S = n_o N\sigma \quad (2)$$

where N is Avogadro's number ($6.02 \cdot 10^{23}$ molecules/mole) and σ is the cross-sectional area of the adsorbate (0.253 nm² for one molecule of CO_2) [49].

2.5.2. Calculation of isosteric heat of adsorption
The characteristic heat of adsorption, E_o, can be related to the isosteric heat of adsorption, Q_{st}, Eq. (3) [3] at the fractional filling ϕ of e^{-1} using the enthalpy of vaporization ΔH_v at the boiling point (17.1548 kJ/mole for CO_2) [47].

$$Q_{st,\phi=e^{-1}} = \Delta H_v + \beta E_o \quad (3)$$

2.5.3. Calculation of average pore size of coals from CO_2 adsorption isotherm
The Dubinin–Astakhov exponent, j, and the characteristic heat of adsorption, E_o, are related to the surface heterogeneity of the adsorbent [40,50]. From these two parameters, the average pore sizes of coals can be calculated from Medek's approach [40,50]:

$$r_e = \frac{(k/E_o)^{1/3}}{\Gamma\left(\frac{3j+1}{3j}\right)} \quad (4)$$

where k (=3.145 kJ nm³ mol⁻¹ for CO_2) is a constant [50] and Γ is the gamma function.

3. Results and discussion

3.1. pH treatment of coals

Eight of the Argonne premium Pocahontas No. 3, Upper Freeport, Pittsburgh No. 8, Lewiston–Stockton, Blind Canyon, Illinois No. 6, Wyodak, and Beulah–Zap coals were treated with dilute acid (H_2SO_4) and dilute base (NaOH) solutions as described in the experimental section. Attempts to similarly treat the Wyodak and Beulah–Zap coals were unsuccessful because the base treatment following the acid treatment resulted in a suspension which could be separated neither *via* filtration through a 45 μm filter nor centrifugation. Therefore, Wyodak and Beulah–Zap coals were excluded from further evaluation.

Table 2 shows the ash content of the pH treated coals. The goal of these experiments was to determine what effect surface charge might have on the adsorption capacity of different coals. In a sequestration environment, the surface charge of the coal would be determined by the liquid phase in contact with it. In this study, pH values of 2, 7, and 10 were chosen as representative of the central and extreme values that might be encountered in a sequestration environment. To differentiate between the effects of mineral dissolution and surface charge, all samples were initially treated with weak acid solution prior to the final pH adjustment. As can be seen, the magnitude of the mineral matter removal was highest at the end of the initial dilute acid and base treatments, and it was the least for the subsequent pH adjustments. For instance, the ash content of Pocahontas No. 3 coal decreased from 4.77% to 3.92% at the end of the initial acid and base treatments. The subsequent pH adjustments reduced the ash content to 3.82% and 3.71% for the neutralization and final acid treatment steps, respectively. The ash content for the Pittsburgh No. 8 was reduced from 9.25% to 8.86%, 8.59%, and 8.42% at the end of the initial acid and base treatment, neutralization, and final acid treatment steps, respectively. Similarly, the ash content for the Illinois No. 6 coal was reduced from 15.48% to 14.55%, 13.30%, and 12.75% at the end of the initial acid and base treatment, neutralization, and final acid treatment steps, respectively. Overall, very little mineral matter was removed from each coal during the pH treatment using dilute acid and base solutions at room temperature and most of the ash content was retained in the coal samples. Although, the magnitude of the mineral matter removal was larger at the end of the initial dilute acid and base treatments, subsequent pH treatments did not prohibit extracting additional inorganics. Thus, considering the isoelectric pH for coals (pH∼3.8) [18], the pH treated coal samples were prepared as negatively charged and positively charged at the end of their final basic and neutral pH treatments, and the acidic treatment, respectively, with small mineral matter removal.

The filtrates of the pH treated coal samples were analyzed for their metal contents. Fig. 2 shows some of the metal contents from the analytical results obtained on the filtrates collected from the
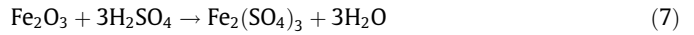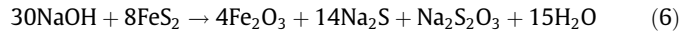
Table 2
Ash content of pH treated coals.

Coals	Ash content (%, moisture free basis)			
	Non-treated	Base washed	Neutralized	Acid washed
Pocahontas No. 3	4.77	3.92	3.82	3.71
Upper freeport	13.18	12.87	12.69	12.43
Pittsburgh No. 8	9.25	8.86	8.59	8.42
Lewiston–Stockton	19.84	18.90	18.79	18.47
Blind Canyon	4.71	4.11	3.75	3.27
Illinois No. 6	15.48	14.55	13.30	12.75

initial acid treatment, base treatment, neutralization, and final acid treatment of the Argonne Premium coals. The initial acid treatment mostly removed calcium (Ca), magnesium (Mg), and iron (Fe). 60–90% of the calcium reported to be in the coal [35] was removed during the initial acid washing and 80–100% of it was removed by the combination of washes. Calcite dissolution is the most likely the source of calcium under acidic conditions.

$$CaCO_3 + H^+ \rightarrow Ca^{+2} + HCO_3^- \qquad (5)$$

Filtrates from the base washing contained mostly potassium (5–40% of the K within the coals). Subsequent neutralization with H_2SO_4 consumed little acid. The filtrates contained basically K, Ca, and Mg. The final acidification removed mostly Fe and some additional Ca, K, and Mg. The behavior of iron is particularly interesting. The samples to show iron extraction upon the initial acidification lends credence to the tentatively reported presence of siderite in these coals [35]. In some cases, iron was not removed during the initial acidification, but was removed during the final acidification

subsequent to the base treatment. In these cases, pyrite (FeS_2) may have been removed according to reactions (6) and (7) [17]. The hematite (Fe_2O_3) formed in reaction (6) is insoluble in base but soluble in acid as shown in reaction (7).

$$30NaOH + 8FeS_2 \rightarrow 4Fe_2O_3 + 14Na_2S + Na_2S_2O_3 + 15H_2O \qquad (6)$$

$$Fe_2O_3 + 3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 3H_2O \qquad (7)$$

Other metals (Mn, P, Sr, Ba, and Mg), when present, are removed in only small amounts (5–10%). Aluminum silicate clays are only slightly reactive toward acidic and basic solutions at low temperatures. However, it should be cautioned that the lack of solubility of a certain mineral under these conditions may not be fully indicative of the dissolution that may occur over prolonged periods. In the current study, equilibration was considered complete when the pH remained constant over 4 hours. In an actual sequestration scenario, contact time may extend for hundreds of years. The equi-
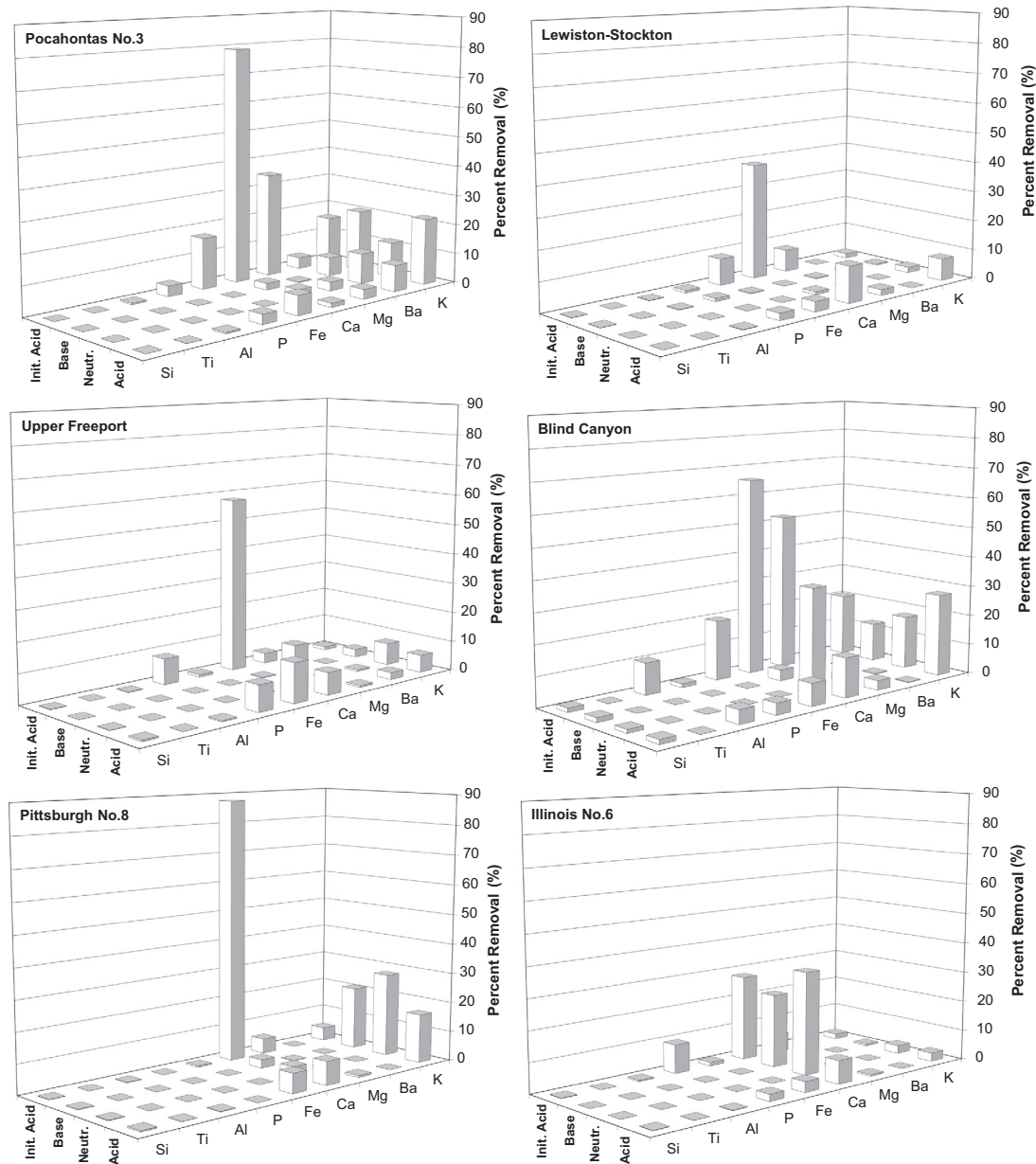

Fig. 2. Analysis of the filtrates collected during the pH treatment of coals.

librium concentrations and the composition of the mineral phases that will ultimately be present are probably predicted better using geochemical models.

3.2. Adsorption Isotherms of CO_2 on pH treated coals

Fig. 3 shows the adsorption isotherms of CO_2 on the pH treated and untreated Argonne Premium Pocahontas No. 3, Upper Freeport, Pittsburgh No. 8, Lewiston–Stockton, Blind Canyon, and Illinois No. 6 coals. The isotherms were measured at 22 °C and pressures up to 4 MPa. The error calculated for the experimental apparatus was less than 3% [11,37,38]. The lines represent the best-fit to the modified Dubinin–Astakhov equation, Eq. (1). As shown in the figure, the excess adsorption isotherms of CO_2 on pH treated coals have similar rectilinear shapes with those of the untreated coals. The difference in the adsorbed amount is small at low pressures for each rank of pH treated and untreated coals whereas the adsorbed amount deviates as pressure increases, especially for medium and low rank coals.

Eq. (1) has been derived to determine the actual adsorbed amount or the absolute adsorption from the excess adsorption isotherms which are confounded due to volumetric inaccuracies caused by phenomenon such as, but not limited to, gas solubility in the solid matrix, to the matrix swelling and shrinkage during the adsorption and desorption experiments, and to over- or under-estimation of the coal volume associated with the adsorp-

tion of helium and/or the sieving effect (see Ref. [37] for the details). The total excess adsorption is dominated by the absolute adsorption term at low pressures indicating that low-pressure adsorption studies (usually less than 0.1 MPa) are relatively free of confounding interferences [38]. However, at higher pressures, such as those of interest to carbon sequestration studies, the unaccounted-for volumetric effects become competitive and eventually they dominate any incremental increases in observed excess adsorption [11,37,38]. Thus, Eq. (1) was employed to interpret the excess adsorption isotherms of CO_2 on coals displayed in Fig. 3.

3.3. CO_2 adsorption capacity of the pH treated argonne coals

Fig. 4 compares the adsorption capacity of CO_2 on the pH treated and untreated coal of each rank obtained from the curve fitting of Eq. (1) to the excess adsorption isotherm data. The adsorption capacities of coal samples increase with increasing ash removal with the sequences of the acid and then the base, neutral, and acidic treatment, respectively. As shown in the figure, the adsorption capacity of CO_2 on base treated coals is generally lower comparing to the untreated coal samples. The adsorption capacity of CO_2 on the neutralized coals is more or less the same with the untreated coals, except for the Illinois No. 6 coal, whereas it is greater for the acid treated coals. Because the removal of mineral matter increases the aperture size of pores and creates extra pore space for adsorption, the removal of the mineral matter from coals
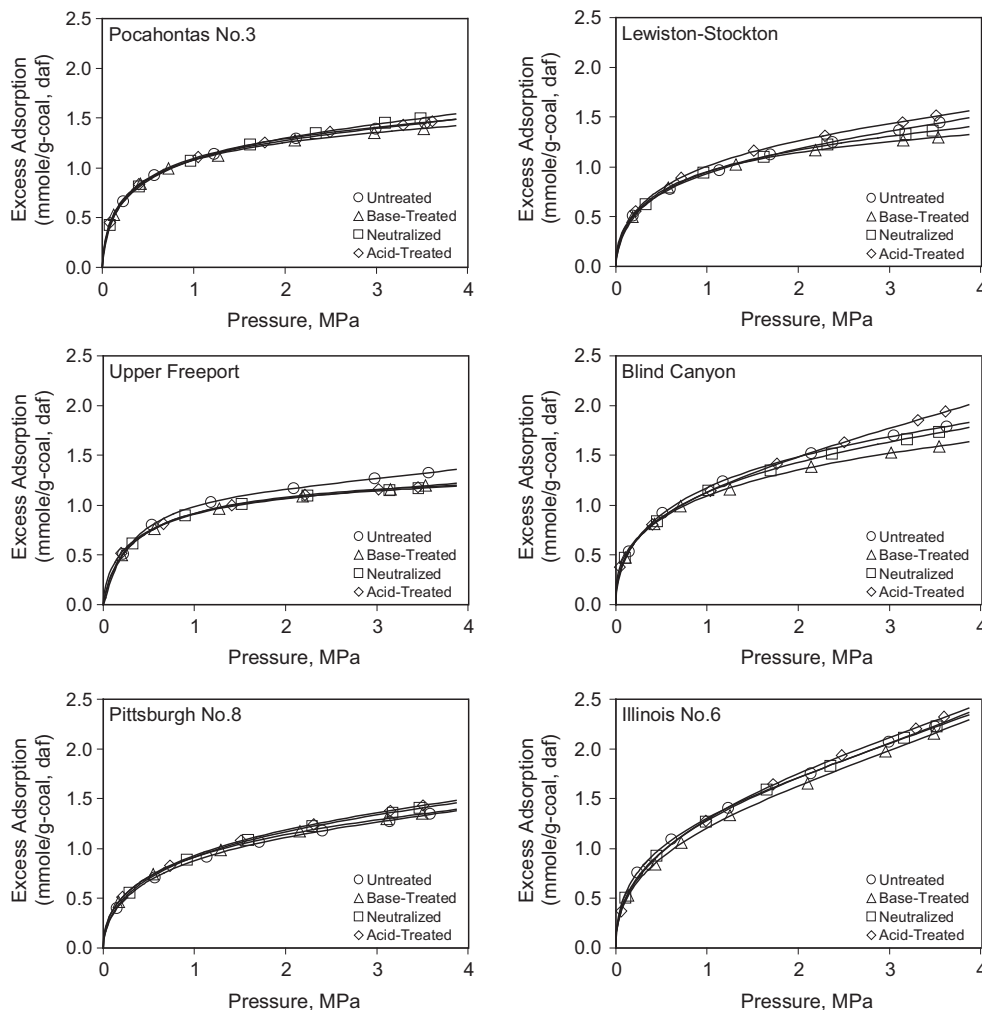

Fig. 3. Adsorption isotherms of pH-treated and untreated Argonne Premium coals.
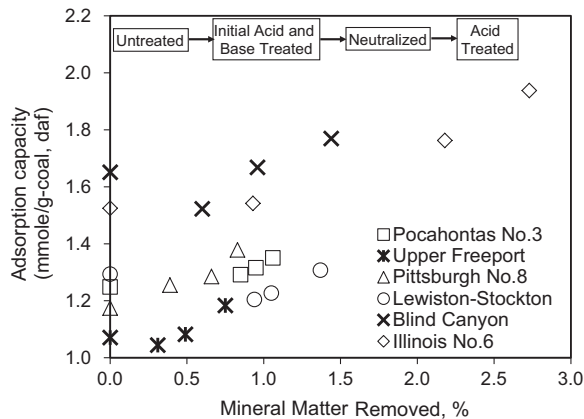
Fig. 4. Adsorption capacity of CO_2 on the pH-treated and untreated Argonne coals.

Fig. 5. Surface area of the pH-treated coals with respect to their rank.

is expected to increase the adsorption capacity of pH treated coals comparing to the untreated coal. This is true for the pH-treated coals such that, as shown in Fig. 4, the adsorption capacity increases as more and more ash is removed from the coals. However, as can be seen from the figure, although the mineral matter removal at the end of the initial acid, and then, the base treatments is bigger than the subsequent neutralization and acid treatment steps, the adsorption capacity of the base treated coals is still lower than that of the untreated coals. The neutralized coals have more or less the same adsorption capacity with the untreated coals even though more mineral matter was removed. The acid treated coals have always higher CO_2 adsorption capacity and higher ash removal compared to base, neutralized, and untreated coals.

The relatively lower adsorption capacity of base treated coals, albeit their ash contents were reduced, may be explained by the effect of the surface charge and its effect on the 3-D structure of coals. At pH greater than the isoelectric point (about 3.8) [18] for coals, most of the coal surface is negatively charged. The removal of the Ca and Mg from the coal structure at the end of acidic and then basic treatment as well as during the neutralization steps may convert the carboxylic groups in their ionic forms. At pH of 2, which is lower than the isoelectric point for coals (about 3.8), most of the coal surface is positively charged. The removal of the Ca and Mg from the coal structure at the end of acidic treatment may convert the carboxylic groups in their protonated forms rather than in their salts. The negatively charged surface would possess stronger surface interactions, which make the coal structure more rigid. Consequently, the 3-D structure of the coal may be affected by the negatively or positively charged surfaces of the coal.

3.4. Surface area of the pH treated argonne coals

The surface areas of the pH treated and untreated Argonne coals were calculated from the CO_2 adsorption capacity using Eq. (2). Fig. 5 compares these calculated surface areas of pH treated coals to the surface areas from the literature, which were calculated from data obtained under more traditional, low-pressure experimental conditions [42]. Because the volumetric effects are small at low pressures, the literature data obtained at low pressures report surface areas which are relatively free of error. The comparison in Fig. 5 shows that the surface area estimated from high pressure adsorption isotherms in Eq. (2) are in good agreement with the low pressure adsorption isotherm values reported by Larsen et al. [42] for the same set of Argonne coals. Only Illinois No. 6 coal failed to give equivalent results, which is mostly due to the different moisture content of coals as indicated by these authors [42]. Good agreement is obtained only if the volumetric effect, ΔV, is
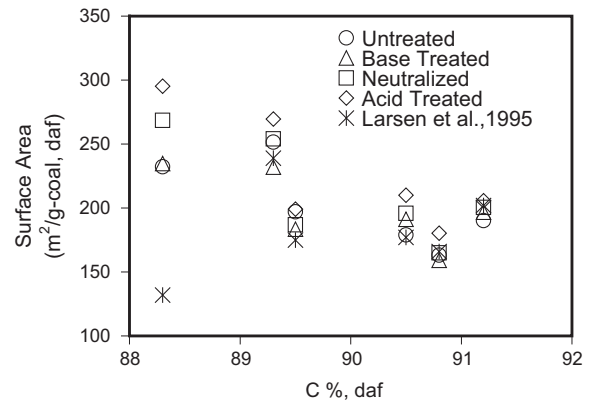
taken into account. When the ΔV effects were not accounted for in the high-pressure data, the estimated surface areas were about 15% to 40% higher for these coals. As shown in the figure, the surface area of the acid treated coals is higher than the base treated, the neutralized, and the untreated coals. The surface area of base treated coals usually lower than the acid treated, and the neutralized coal while the neutralized coals follow similar trend with the untreated coals.

3.5. Isosteric heat of adsorption

Fig. 6 shows the isosteric heat of adsorption of CO_2 on the pH treated and untreated coals. As shown in the figure, the isosteric heat of adsorption is generally higher for the base treated coals compared to the acid treated, neutralized, and untreated coals. The isosteric heat of adsorption is generally similar for the neutralized and untreated coals whereas the isosteric heat of adsorption is generally lower for the acid treated coals. The literature data related to the isosteric heat of adsorption of pH treated coals is limited for comparison. Here, the agreement between the isosteric heat of adsorption obtained for the Illinois No. 6 using the modified D-A equation, Eq. (2), and that reported by Glass and Larsen [51] using the inverse gas chromatography is in excellent agreement. The range and magnitude of these values suggests a physical-adsorption mechanism rather than a chemisorption mechanism.

It is recognized that the heat of adsorption is related to the degree of interaction between the adsorbed CO_2 and the chemical groups on the surfaces of the coal as well as the pore size of the coal [40,51]. Therefore, the higher isosteric heat of adsorption for
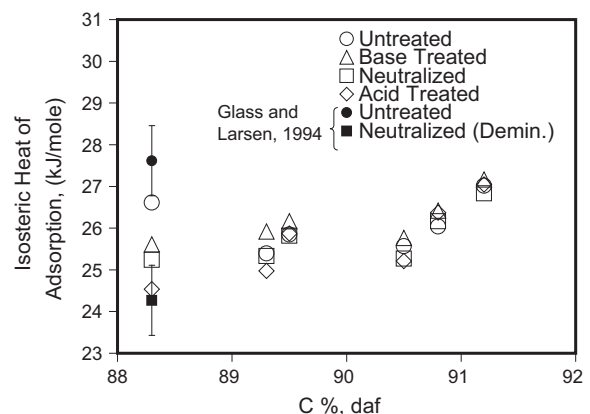

Fig. 6. Characteristic heat of CO_2 adsorption on pH-treated Argonne Premium coals.

the base treated coals may be due to the stronger interaction of CO_2 with the negatively charged surface groups such as ionized carboxylic and deprotonated amine groups [32]. Or, as will be shown next, the higher isosteric heat of adsorption may be due to the narrower pore sizes resulted in the pH treatment of coals. A wider pore volume requires a low isosteric heat of adsorption, and a narrower pore size requires a higher isosteric heat of adsorption due to overlapping the surface potential of a pore [48].

3.6. Average pore size of the pH treated argonne coals reported by CO_2

The adsorption of CO_2 can be used to characterize the microporous structure of coals [48,52,53]. The Dubinin–Astakhov exponent, j, and the characteristic heat of adsorption, E_o, are related to the surface heterogeneity of the adsorbent [40,50]. From these two parameters, the average pore size of a porous adsorbent, r_e, can be calculated from Medek's approach [40,50]. Fig. 7 shows the average pore size of the pH treated and untreated coals. As shown in the figure, the average pore size for the base treated coals is generally lower comparing to the acid treated, the neutralized, and the untreated coals. The pore sizes are generally similar for the neutralized, and untreated coals. On the other hand, the average pore size for the acid treated coals is generally higher comparing to that of the base treated, neutralized and untreated coals. The data suggest that removal of ash from coals creates extra pore space in pH treated coals, which, as discussed earlier, affects both the adsorption capacity and the isosteric heat of adsorption of CO_2 on coals.

3.7. Volumetric effects

Fig. 8 shows the volume changes estimated from the adsorption isotherm measurement over the 4 MPa range. As discussed in our previous papers [11,37,38], the ΔV term in Eq. (1) results from either the volumetric changes due to the solubility of CO_2 in the solid coal matrix, to the swelling and shrinkage of coals during the adsorption isotherm measurements, as well as to any over- or under-estimation of the skeleton volume of the coal due to the adsorption of He and/or the sieving effect between the He and CO_2. This volume effects are the origin of the rectilinear shape of the adsorption isotherm at high pressures. When these volume changes were not considered in the evaluation of the adsorption isotherm data, the estimated values of the physical constants in the absolute adsorption model equation were overestimated [38]. As shown in the figure, magnitude of the volume effects for the pH treated coals are generally less than the volume effects obtained for the untreated coals. The less volume change may indicate maintaining a more rigid 3-D structure of the coal.
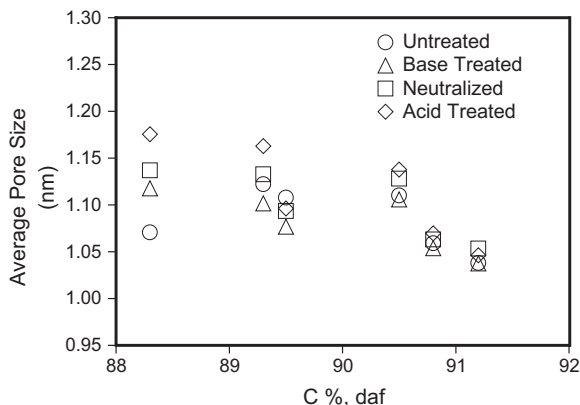

Fig. 7. Average pore sizes of pH-treated coals estimated from CO_2 adsorption isotherms at 22 °C.
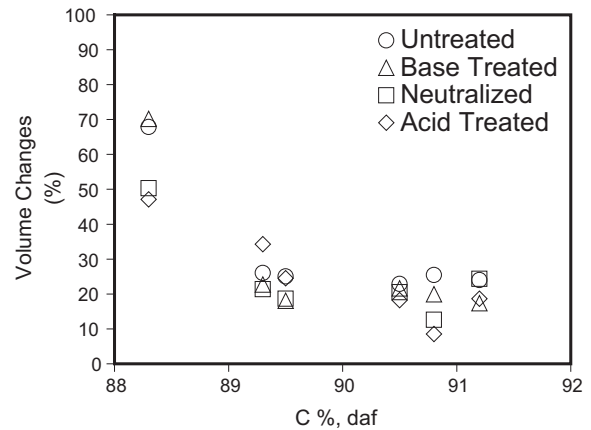

Fig. 8. Estimated volume change during the adsorption measurements at 4 MPa.

Even if initially dry, the coal seam will certainly become wet as a result of drilling operations, fracturing of the coal bed and overlying strata, and the deposition of a combustion gas which may contain residual water of combustion. Thus, an aqueous phase will be present and will vary in composition according to its source and the nature of the coal bed and the surrounding minerals with which it is in contact. In natural systems, pH is often an important parameter [54] and it will change during sequestration. Because of the formation of carbonic acid, the pH within the sequestration media will drop up to around 3 at high CO_2 pressures, favoring the dissolution of calcite. This may be beneficial if mineral dissolution provides better access to the organic matrix, but would be detrimental if dissolution of cap-rock resulted [8,55]. The effect of the sequestration on pH would be more dramatic for those scenarios in which the SO_x and NO_x were not removed by prior separation and are sequestered along with the CO_2 [10].

It has long been known that coal is an excellent substrate for gas adsorption. Studies have shown that the capacity that coals adsorb CO_2 is higher than the gases such as N_2 and CH_4 [56]. The adsorption capacity is dependent on the nature of the coal itself such as rank and moisture content of coals and the sequestration environment such as temperature and pressure. It has been shown in this study that pH could also be an important environmental parameter. It directly affects the mineral matter content, the surface charge, and the associative characteristics of the layered structure of the coal matrix.

4. Conclusion

Sequestration of CO_2 in unmineable coal seams has been proposed one of the geologic strategies to mitigate the increasing concentrations of CO_2 in the atmosphere. Injection of CO_2 into wet coal seams will certainly result in the dissolution of CO_2 in water and reduce the pH within the cleat system surrounding the coal matrix. There are two consequences of pH variation in coal seams. One is the dissolution of mineral matter in coal, and the other is the alteration of its surface charge. The extraction of minerals from a coal is expected to increase the surface area of the organic matrix available for CO_2 adsorption. Also, acidic pHs would cause to increase the adsorption capacity by removing the mineral matter from the pores entrances which block the pore apertures. As a matter of fact while acidic pHs favor the enhanced CO_2 storage capacity, basic pHs seemed to disfavor it because the negatively charged surface seems to maintain a more rigid structure of coals with smaller pores. Therefore, it is concluded that the pH decrease due to CO_2 dissolution in cleat water is favored in coal seam sequestration, which resulted in an increase in storage capacity of coals.

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Acknowledgements

References

[1] Busch A, Gensterblum Y. CBM and CO_2-ECBM related sorption processes in coal: a review. Int J Coal Geol 2011;87:49–71.

[2] White CM, Smith DH, Jones KL, Goodman AL, Jikich SA, LaCount RB, et al. Sequestration of carbon dioxide in coal with enhanced coalbed methane recovery – a review. Energy Fuels 2005;19:659–724.

[3] Aoshima M, Fukasawa K, Keneko K. Micropore filling of supercritical Xe in micropores of activated carbon fibers. J Colloid Interface Sci 2000;222:179–83.

[4] Karacan CO. Swelling-induced volumetric strains internal to a stressed coal associated with CO_2 sorption. Int J Coal Geol 2007;72:209–20.

[5] Karacan CO, Okandan E. Adsorption and gas transport in coal microstructure: investigation and evaluation by quantitative X-ray CT imaging. Fuel 2001;80:509–20.

[6] Wei XR, Wang G, Massarotto P, Golding SD, Rudolph V. Numerical simulation of multicomponent gas diffusion and flow in coals for CO_2 enhanced coalbed methane recovery. Chem Eng Sci 2007;62:4193–203.

[7] Weishauptova Z, Pribyl O, Sykorova I, Machovic V. Effect of bituminous coal properties on carbon dioxide and methane high pressure sorption. Fuel 2015;139:115–24.

[8] Gaus I. Role and impact of CO_2-rock interactions during CO_2 storage in sedimentary rocks. Int J Coal Geol 2010;4:73–89.

[9] Day S, Fry R, Sakurovs R. Swelling of moist coal in carbon dioxide and methane. Int J Coal Geol 2011;86:197–203.

[10] Crandell LE, Ellis BR, Peters CA. Dissolution potential of SO_2 co-injected with CO_2 in geologic sequestration. Environ Sci Technol 2010;44:349–55.

[11] Ozdemir E, Schroeder K. Effect of moisture on adsorption isotherms and adsorption capacities of CO_2 on coals. Energy Fuels 2009;23:2821–31.

[12] Bustin M. Research activities on CO_2, H_2S, and SO_2 sequestration at UBC. Coal-Seq I Forum. Houston, TX2002.

[13] Schroeder K, Ozdemir E, Morsi BI. Sequestration of carbon dioxide in coal seams. First national carbon sequestration conference proceeding; 2001. U.S. DOE/NETL:1–10.

[14] Day S, Duffy G, Sakurovs R, Weir S. Effect of coal properties on CO_2 sorption capacity under supercritical conditions. Int J Greenhouse Gas Control 2008;2:342–52.

[15] Ozdemir E. Chemistry of the adsorption of carbon dioxide by Argonne premium coals and a model to simulate CO_2 sequestration in coal seams [Ph.D. Dissertation]. Pittsburgh: University of Pittsburgh; 2004.

[16] Hayashi J, Takeuchi K, Kusakabe K, Morooka S. Removal of calcium from low rank coals by treatment with CO_2 dissolved in water. Fuel 1991;70:1181–6.

[17] Kumar M, Shankar RH. Removal of ash from Indian Assam coking coal using sodium hydroxide and acid solutions. Energy Sources 2000;22:187–96.

[18] Labuschange BCJ. Relationship between oil and agglomaration and surface properties of coal: effect of pH and oil compositition. Coal Prep 1986;3:1–13.

[19] Sakanishi K, Watanabe I, Nonaka T, Kishino M, Mochida I. Effects of organic acid pretreatment on the structure and pyrolysis reactivity of coals. Fuel 2001;80:273–81.

[20] Larsen JW. The effects of dissolved CO_2 on coal structure and properties. Int J Coal Geol 2004;57:63–70.

[21] Larsen JW, Pan CS, Shinn JH. Effect of demineralization on the macromolecular structure of coals. Energy Fuels 1989;3:557–61.

[22] Mahajan OP. Coal porosity. In: Meyers RA, editor. Coal structure. New York: Academic Press; 1982. p. 51–86.

[23] Harvey RD, Ruch RR. Mineral matter in Illinois and other U.S. coals. In: Vorres KS, editor. Mineral matter and ash in coal. Washington, D.C.: American Chemical Society; 1986. p. 10–40.

[24] Hendrics TA. The origin of coal. Chem Coal Util 1945:1–24.

[25] Finkelman RB, Stanton RW. Identification and significance of accesory minerals from a bituminious coal. Fuel 1978;57:763–8.

[26] Thiessen G. Forms of sulphus in coal. In: Lowry HH, editor. Chemistry of coal utilization; 1945. p. 425–49.

[27] Joseph JT, Forrai TR. Effect of exchangable cations on liquification of low rank coals. Fuel 1992;71:75–80.

[28] Kirner WR. The occurence of nitrogen in coal. In: Lowry HH, editor. Chemistry of coal utilization; 1945. p. 450–84.

[29] Chen C, Gao J, Yan Y. Role of noncovelent bonding in swelling of coal. Energy Fuels 1998;12:1328–34.

[30] Larsen JW, Green TK, Kovac J. Nature of the macromolecular network structure of bituminious coals. J Org Chem 1985;50:4729–35.

[31] Mahajan OP, Walker PL. Effect of inorganic matter removal from coals and chars on their surface areas. Fuel 1979;58:333–7.

[32] Nishino J. Adsorption of water vapor and carbon dioxide at carboxylic functional groups on the surface of coal. Fuel 2001;80:757–64.

[33] Goodman AL. A Comparison study of carbon dioxide adsorption on polydimethylsiloxane, silica gel, and illinois no. 6 coal using in situ infrared spectroscopy. Energy Fuels 2009;23:1101–6.

[34] Goodman AL, Campus LA, Schroeder KT. Direct evidence of carbon dioxide sorption on argonne premium coals using attenuated total reflectance-fourier transform infrared spectroscopy. Energy Fuels 2005;19:471–6.

[35] Vorres KS. User's Handbook for the Argonne premium coal sample program. Illinois: Argonne National Laboratory; 1993.

[36] Schmidth LD. Changes in coal during storage. In: Lowry HH, editor. Chemistry of coal utilization; 1945. p. 627–76.

[37] Ozdemir E, Morsi BI, Schroeder K. Importance of volume effects to adsorption isotherms of carbon dioxide on coals. Langmuir 2003;19:9764–73.

[38] Ozdemir E, Morsi BI, Schroeder K. CO_2 adsorption capacity of argonne premium coals. Fuel 2004;83:1085–94.

[39] Span R, Wagner W. A new equation of state for carbon dioxide covering the fluid region from tripple-point temperature to 1100 K at pressures up tp 800 MPa. J Phys Chem Ref Data 1996;25:1509–96.

[40] Medek J. Possibility of micropore analysis of coal and coke from the carbon dioxide isotherm. Fuel 1977;56:131–3.

[41] Karacan CO. Heterogeneous sorption and swelling in a confined and stressed coal during CO_2 injection. Energy Fuels 2003;17:1595–608.

[42] Larsen JW, Hall P, Wernett PC. Pore structure of the argonne premium coals. Energy Fuels 1995;9:324–30.

[43] Malbrunot P, Vidal D, Vermesse J. Adsorbent helium density measurement and its effect on adsorption isotherms at high pressure. Langmuir 1997;13:539–44.

[44] Romanov VN, Goodman AL, Larsen JW. Errors in CO_2 adsorption measurements caused by coal swelling. Energy Fuels 2006;20:415–6.

[45] Sakurovs R, Day S, Weir S, Duffy G. Application of a modified Dubinin–Radushkevich equation to adsorption of gases by coals under supercritical conditions. Energy Fuels 2007;21:992–7.

[46] Sircar S. Gibbsian surface excess for gas adsorption-revisited. Ind Eng Chem Res 1999;38:3670–82.

[47] Reid RC, Prausnitz JM, Sherwood TK. The properties of gases and liquids. 3rd ed. McGraw Hill; 1977.

[48] Dubinin MM. The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces. Chem Rev 1960;60:234–41.

[49] Levy JH, Day SJ, Killingley JS. Methane capacities of Bowen basin coals related to coal properties. Fuel 1997;76:813–9.

[50] Debelak KA, Schrodt JT. Comparison of pore structure in Kentucky coals by mercury penetration and carbon dioxide adsorption. Fuel 1979;58:732–6.

[51] Glass AS, Larsen JW. Coal surface properties. specific and nonspecific interactions for polar molecules and surface tensions for hydrocarbons at the surface of Illinois No. 6 coal. Energy Fuels 1994;8:629–36.

[52] Aranovich GL, Donohue MD. Adsorption isotherms for microporous adsorbents. Carbon 1995;33:1369–75.

[53] Gil A, Grange P. Application of the Dubinin–Radushkevich and Dubinin–Astakhov equations in the characterization of microporous solids. Colloids Surf A-Physicochem Eng Aspects 1996;113:39–50.

[54] Stumm W, Morgan JJ. Aquatic chemistry: chemical equilibria and their rates in natural waters. New York: John Willey & Sons; 1996.

[55] Knauss KG, Johnson JW, Steefel CI. Evaluation of the impact of CO_2, co-contaminant gas, aqueous fluid and reservoir rock interactions on the geologic sequestration of CO_2. Chem Geol 2005;217:339–50.

[56] DeGance AE, Morgan WD, Yee D. High pressure adsorption of methane, nitrogen and carbon dioxide on coal substrates. Fluid Phase Equilib 1993;82:215–24.

[57] Vorres KS. The Argonne premium coal sample program. Energy Fuels 1990;4:420–6.