RELATIONSHIP OF SORPTION CAPACITY TO COAL QUALITY: CO_2 SEQUESTRATION POTENTIAL OF COALBED METHANE RESERVOIRS IN THE BLACK WARRIOR BASIN

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Abstract

The relationship between coal quality and gas sorption was studied as part of an investigation of the CO_2 sequestration and enhanced coalbed methane recovery potential of the Black Warrior basin. Of the coal quality parameters analyzed, rank and mineral matter content are the most important controls on sorption capacity, whereas maceral composition is of limited significance. Coal rank in the coalbed methane fields ranges from high-volatile B bituminous to low-volatile bituminous, and sorption capacity increases significantly with rank. Although the rank of a given coal bed varies regionally, local variation is minimal, and rank values can be interpolated between control points with confidence. The distribution of mineral matter, by comparison, is difficult to predict. For example, ash content in a single coal bed can change by more than 20% in less than 0.5 mi, and local variability far exceeds any discernible regional trends. A weak positive correlation was found between ash content and sorption capacity because of poor sorption performance in coal with less than 5% ash. For coal with more than 5% ash, sorption capacity and ash content are negatively correlated.

Introduction

Coal quality parameters, including maceral composition, grade, and rank, have a significant impact on the source rock and reservoir characteristics of coal (e.g., Kim, 1977; Levine, 1993; Lamberson and Bustin, 1993; Bustin and Clarkson, 1998). The Black Warrior basin contains mature coalbed methane reservoirs that have produced more than 1.3 Tcf of gas from the Lower Pennsylvanian Pottsville Formation (fig. 1). A significant coalbed gas resource may remain untapped, and potential exists for CO_2 sequestration and enhanced coalbed methane recovery through injection of CO_2 derived from the flue gas of coal-fired power plants (Pashin et al., 2001, 2003). The ability of coal in the Black Warrior coalbed methane fields to sorb gas is highly variable (fig. 2), and much of this variability may be related to differences of coal quality. This report focuses on the relationship of coal quality to gas sorption in the Black Warrior basin to help explain this variability and to quantify the CO_2 sequestration capacity of Pottsville coalbed methane reservoirs.

To determine the relationship between coal quality and gas sorption capacity, 26 coal samples were collected from exploration cores donated by Jim Walter Resources Incorporated and El Paso Energy Corporation and from active coal mines. The location, depth, and thickness of all sampled coal beds were recorded, and the samples were placed into air-tight plastic bags and numbered. Next, all samples were crushed to -10 mesh. A split of 50 to 200 g was taken for archival collection purposes and stored in an airtight plastic bag. Another split of about 20 to 30 g was crushed to -20 mesh and placed into paper coin envelopes. Each -20 split was used to make polished epoxy pellets, and vitrinite reflectance and maceral composition were determined with a reflected light microscope using standard procedures.

Samples larger than 500 g were sent to Alabama Power Company for proximate and ultimate analysis, and at least 300 g were sent to RMB Earth Science Associates, where isotherms were run for CO_2, CH_4, and N_2,, which are the principal gases in coal and flue gas. Because of the quantity of coal required, only beds thicker than 18 inches were analyzed. Proximate and ultimate analyses were carried out according to ASTM standards except for moisture, which requires more sample than was available.

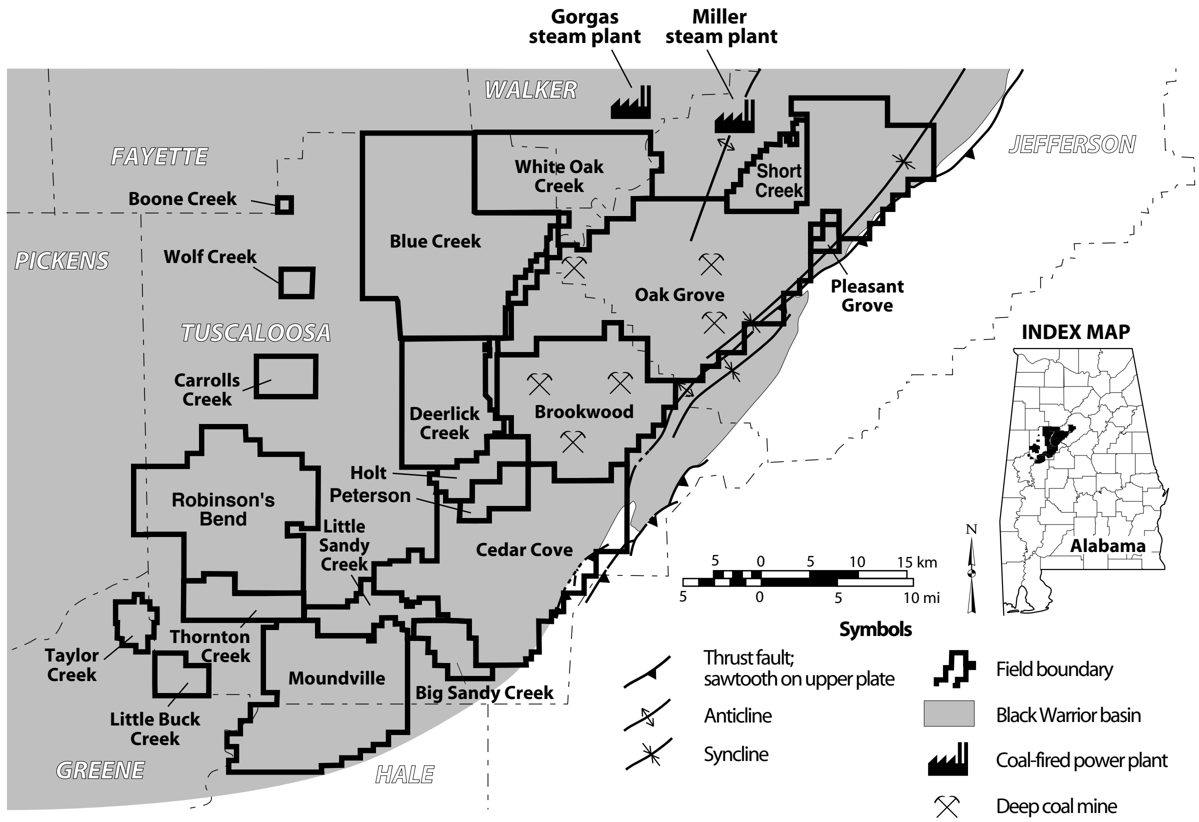

Figure 1. Index map of the eastern Black Warrior basin in Alabama showing locations of coalbed methane fields, underground coal mines, coal-fired power plants, and Appalachian folds and thrust faults (after Pashin et al., 2001).

Samples for isotherm analysis were crushed to -60 mesh and placed in a bath to bring the samples to equilibrium moisture. Equilibrium moisture and ash content were determined on a two-gram split of each sample. Each sample was then split into three subsamples, and high-pressure sorption isotherms were run at 80°F using an apparatus and methodology similar to that described by Mavor et al. (1990). A temperature of 80°F was chosen because it approximates reservoir temperature near the active coal-fired power plants (Pashin and McIntyre, this volume). Finally, data from the isotherms were plotted against maceral composition, grade parameters, and rank to quantify the influence of coal quality on sorption capacity. Many of the basic data used in this report are tabulated in Pashin et al. (2003).

Maceral Content

The bright-banded coal of the Black Warrior basin is rich in vitrinite (70-95%) and contains subordinate amounts of inertinite (5-30%) and liptinite (0-8%) (fig. 3). The coal can generally be classified as bimacerite, or more specifically, vitrinertite, and petrologic analyses of coal from the cores sampled in this study are consistent with other analyses of Alabama coal (e.g., Telle and Thompson, 1987). Two varieties of vitrinite are abundant in the samples analyzed. Telovitrinite, which is the purest form of vitrinite, constitutes about 60% of the vitrinite in most samples. Detrovitrinite, which can contain inclusions of other macerals such as sporinite and fusinite, forms about 40% of the total vitrinite in the samples analyzed.

The high vitrinite content and extremely low liptinite content of coal in the Black Warrior basin (fig. 3) suggests that it is a gas-prone source rock. Vitrinite is generally thought to be the principal gas-sorbent maceral in coal, although Levine (1993) indicated that the relationship of gas sorption to maceral composition can be difficult to predict. Indeed, correlating sorption capacity with total vitrinite content

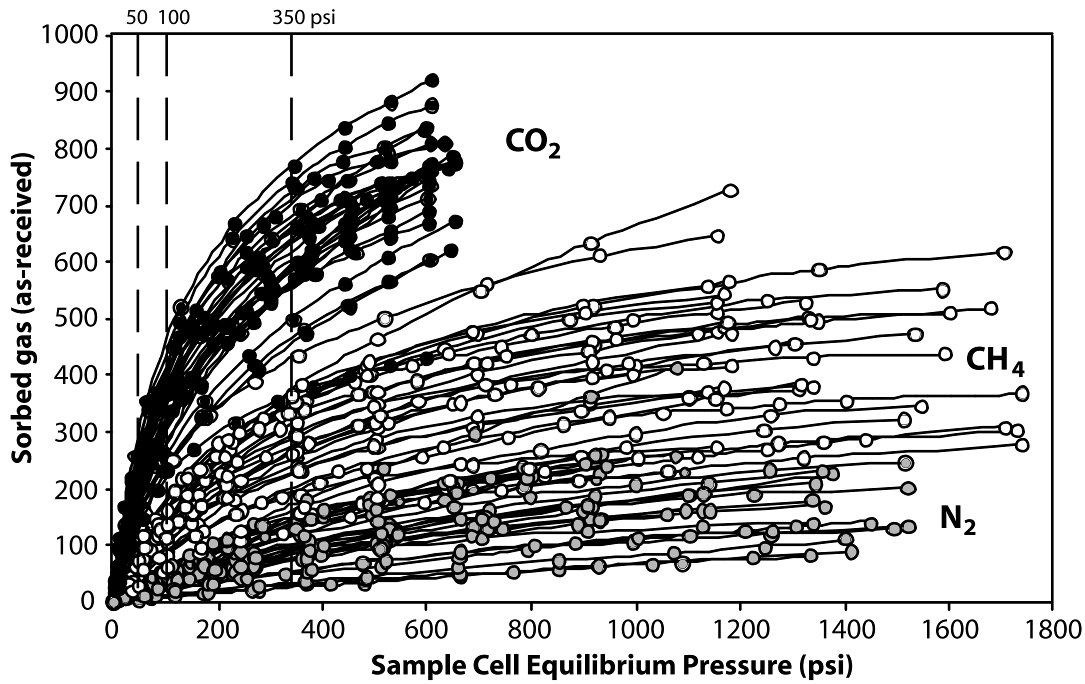

Figure 2. Sorption isotherms for CO_2, CH_4, and N_2 in 26 coal samples from the Black Warrior basin.

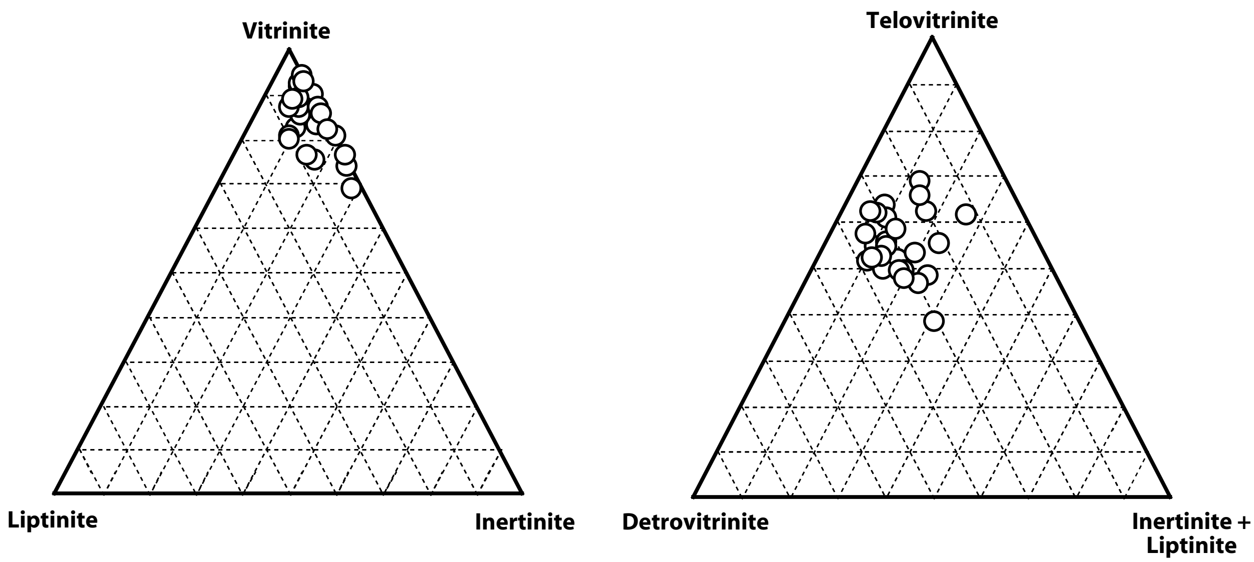

Figure 3. Ternary plots showing the maceral composition of coal samples used for isotherm analysis.

yields a regression coefficient of only 0.03 for CO_2 (fig. 4). However, when sorbed gas is plotted against the percentage of telovitrinite, a weak positive correlation emerges (r = 0.21). Regardless, maceral composition is a poor predictor of the sorption performance of coal in the Black Warrior basin, and the effect of this variable may be masked by variation of grade and rank.

Grade

The major grade parameter affecting the sorption capacity of coal is mineral matter content. The dominant forms of mineral matter in Alabama coal are clay minerals, quartz, pyrite, and calcite, and more than 850 proximate and ultimate analyses are available to analyze key grade parameters (Bragg et al., 1998). These analyses report ash, which includes the non-combustible residue of mineral matter, and sulfur forms, which include pyritic sulfur and organic sulfur.

In the Alabama Pottsville, ash content is characteristically between 2 and 30 percent (Shotts, 1956, 1960; Winston, 1990a). A histogram of ash content confirms this and demonstrates that ash values can be characterized as a normal population with positive skewness (fig. 5). Mean ash content is 12 percent, and values between 6 and 18 percent fall within one standard deviation of the mean. Comparison of ash content in the Mary Lee and Utley coal beds in Blue Creek Field underscores the extreme variability of ash content within and among coal beds (fig. 6).

Although the relative proportions of clay and quartz in the mineral matter fraction of coal cannot be determined from proximate and ultimate analyses, ultimate analysis enables quantification of sulfur and pyrite content in coal. Total sulfur content determined from coal of the Black Warrior basin ranges from 0.2 to 10.5 percent, and sulfur values form a log-normal distribution with weak positive skewness (fig. 4). Mean sulfur content as calculated on a log-normal basis is 1.65 percent, and values between 0.8 and 2.3 percent fall within one standard deviation from the mean. Organic sulfur content has a strong central tendency about a log-normal mean of 0.6 percent and is nearly invariant with respect to total sulfur, whereas pyritic sulfur is the principal determinant of total sulfur content (Pashin et al., 2003). An important point to consider is that the specific gravity of pyrite is about 2.4 times as great as that of elemental sulfur, thus pyrite makes a proportionally greater contribution to total coal composition than pyritic sulfur as reported in ultimate analyses.

In the samples studied, no correlation or weak correlations exists between ash content and sorption capacity (fig. 7). CO_2 capacity is not correlated with ash content, whereas CH_4 and N_2 capacity are positively correlated (r = 0.24 and 0.30, respectively). Examination of the scatterplots indicates that data points tend to be widely scattered and that the positive correlation is chiefly a function of poor sorption performance below 5 percent ash and exceptional performance of one sample with 23 percent ash. If regression analysis is performed only on samples with 5 to 21 percent ash, a negative correlation is found (fig. 8). This correlation is strongest for CO_2 (r = -0.48) and weakest for N_2 (r = -0.17).

Rank

Major rank parameters in coal include volatile matter content, fixed carbon content, calorific value, moisture, and vitrinite reflectance. Multiple rank parameters have been mapped for each Pottsville coal zone by Winston (1990a, b), and most recent work has relied on mapping and interpretation of volatile matter and vitrinite reflectance data (Telle et al., 1987; Winston, 1990a, b; Levine and Telle, 1991; Pashin et al., 2003). Coal rank in the study area ranges from high volatile B bituminous to low volatile bituminous (Semmes, 1929; Winston, 1990a, b) (fig. 9), and to date, virtually all coalbed methane production in Alabama is from coal of high volatile A bituminous rank or higher.

In the Mary Lee coal zone, high volatile B bituminous coal is in the western part of the production fairway in a corridor between Robinson’s Bend and Deerlick Creek fields, and extending northward along the western margin of Blue Creek Field. Most coal in the gas production fairway is of high volatile A bituminous rank, and an elliptical area containing medium volatile and low volatile bituminous coal of metallurgical quality is centered near the southeast margin of the basin in Oak Grove and Brookwood fields.

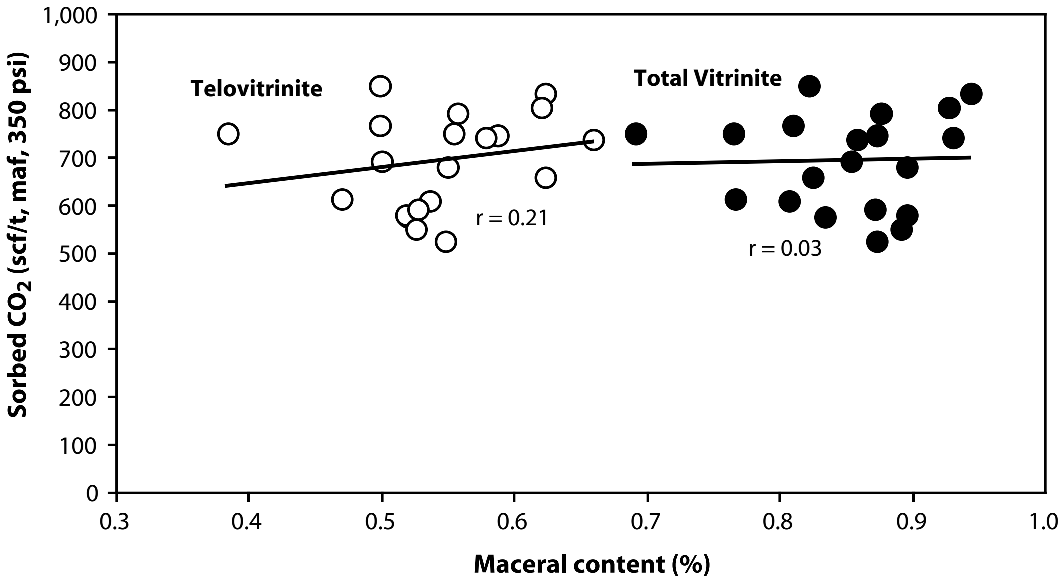

Figure 4. Scatterplots showing relationship of maceral content to sorption capacity.

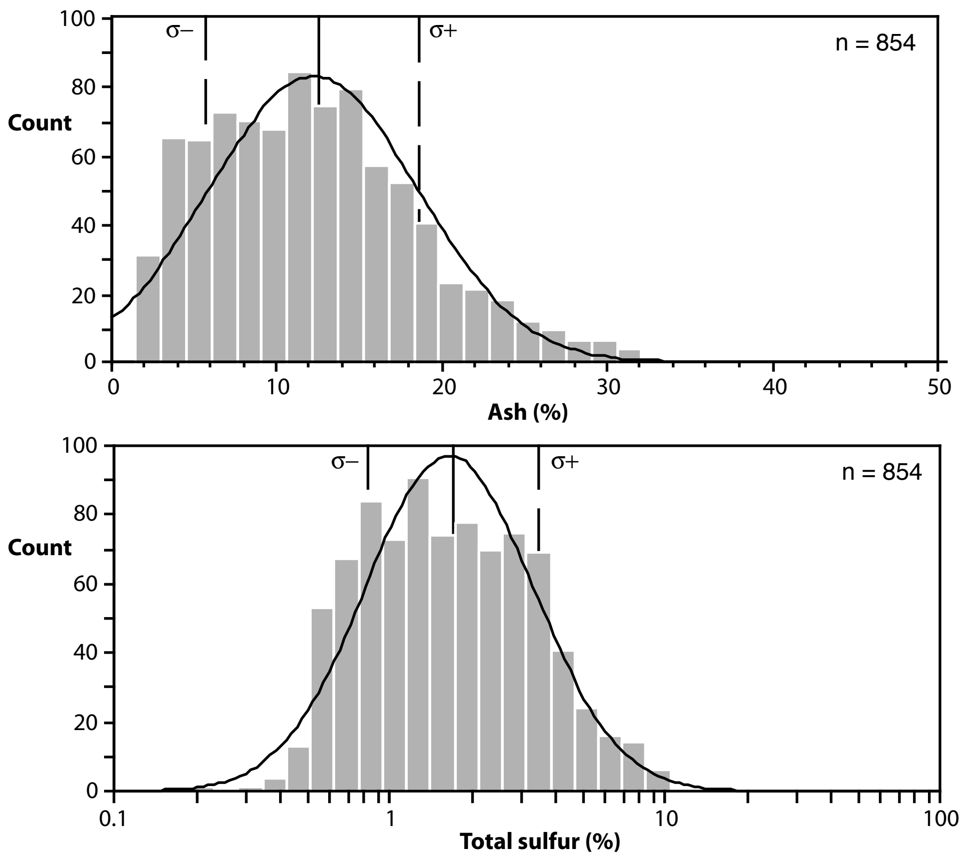

Figure 5. Histograms of ash and sulfur content in coal of the Black Warrior basin.

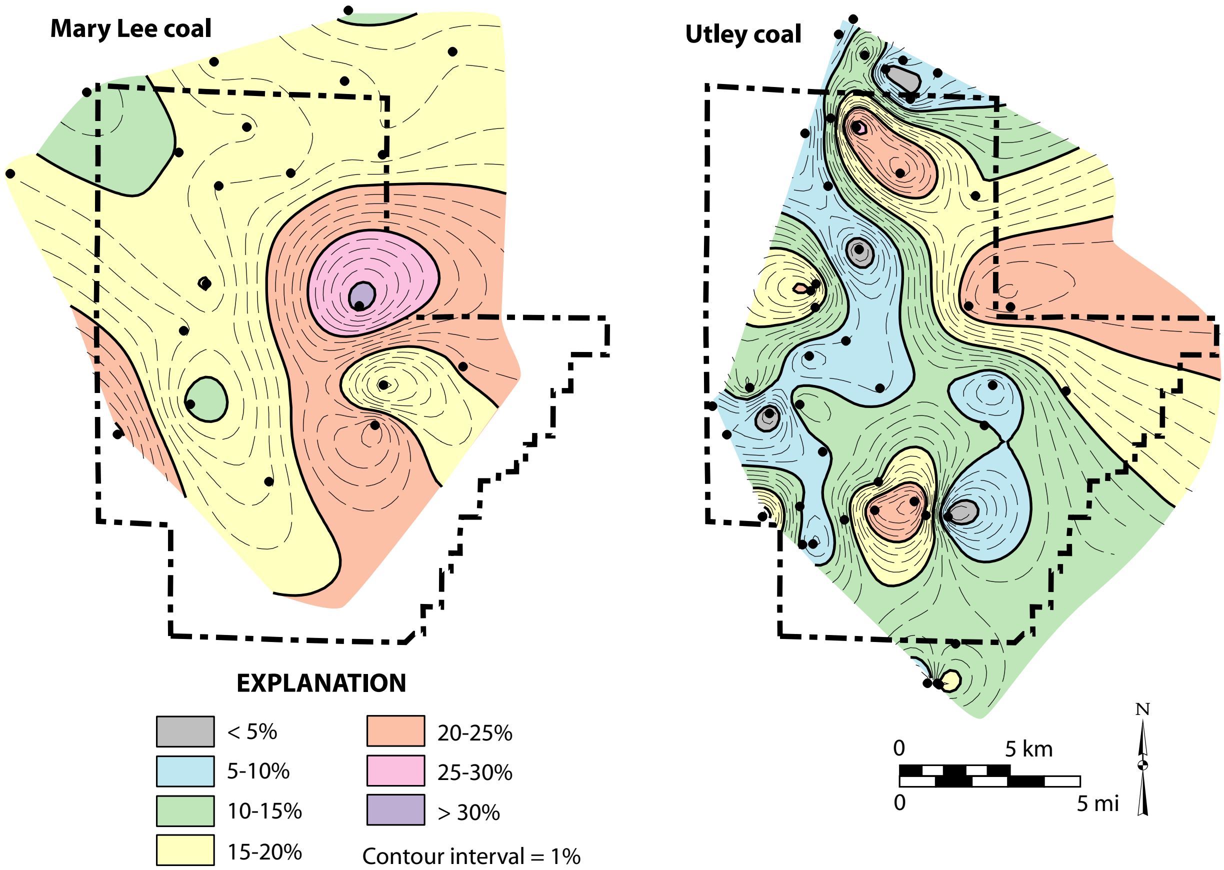

Figure 6. Maps of ash content in the Mary Lee and Utley coal beds, Blue Creek Field.

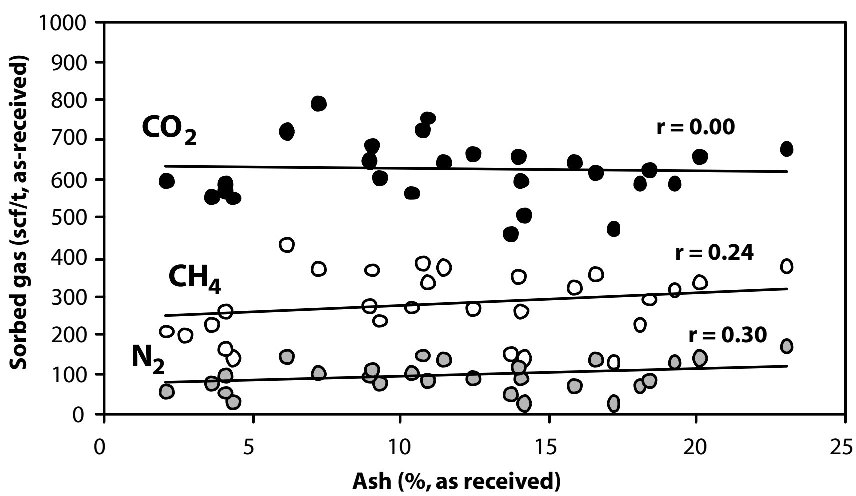

Figure 7. Scatterplot showing relationship between sorption capacity and ash content in coal of the Black Warrior basin.

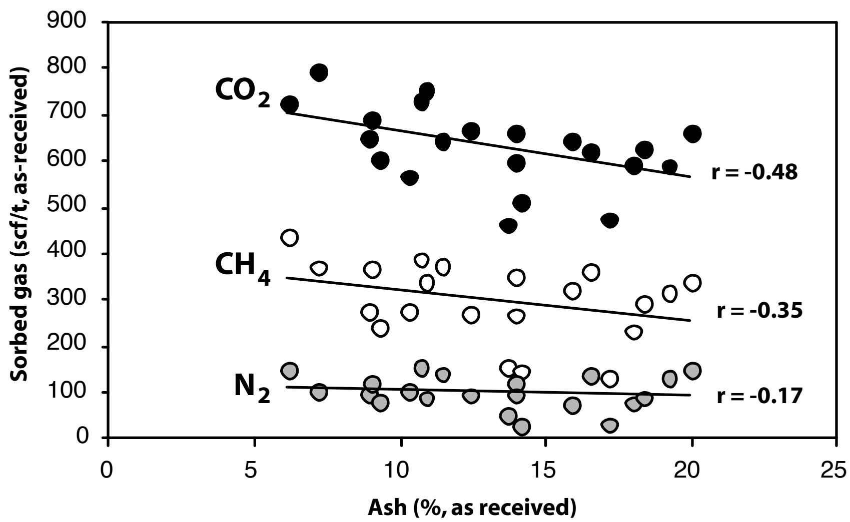

Figure 8. Scatterplot showing negative correlation between sorption capacity and ash content for coal samples with 5 to 21 percent ash.

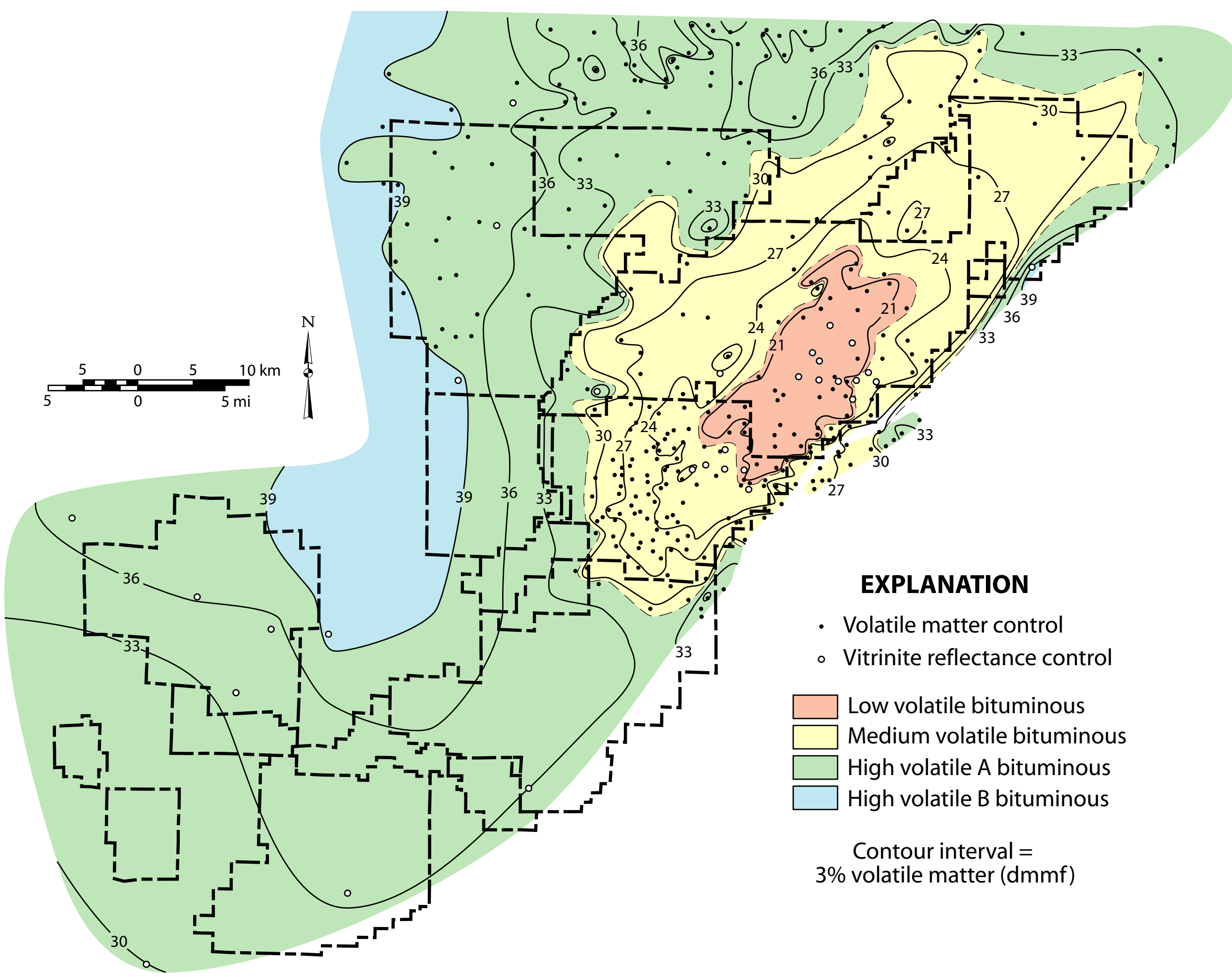

Figure 9. Map of coal rank in the Mary Lee coal zone based on volatile matter and vitrinite reflectance data.

The samples analyzed range in rank from high volatile A bituminous to medium volatile bituminous (fig. 10). Regression analysis demonstrates a significant negative correlation between sorption capacity and volatile matter content. N_2 and CH_4 are most strongly correlated with volatile matter content (r = -0.88 and -0.87, respectively), whereas CO_2 is less strongly correlated (r = -0.68). These results indicate that rank is a dominant control on the gas sorption capacity of coal in the Black Warrior basin. However, sorption of CO_2 is less dependent on rank than is sorption of the other gases analyzed in this investigation.

Discussion

Understanding the gas sorption capacity of coal is extremely important when considering CO_2 sequestration and enhanced recovery projects because injection operations may result in complete isothermal saturation of coal with CO_2. Exceeding the sorption capacity, moreover, may result in leakage of gas into the country rock and ultimately back to the surface. The three gases that come into play in carbon sequestration and enhanced coalbed methane recovery are CO_2, which is the greenhouse gas to be sequestered, CH_4, which is the objective of enhanced coalbed methane recovery, and N_2, which is the dominant constituent of the gas emission stream from coal-fired power plants. Importantly, both CO_2 and N_2 both have potential to drive enhanced coalbed methane recovery (Puri and Yee, 1990).

Isotherms for all three gases indicate that the sorption performance of coal for each gas studied can vary by a factor greater than 2 on as-received basis (fig. 2). These results are in keeping with those of previous investigators, who found that coal sorbs significantly more CO_2 than CH_4 or N_2 (Arri et al., 1992; Harpalani and Pariti, 1993; Hall et al., 1994). Interestingly, the three gases show little overlap in overall sorption performance. Isotherms from individual coal samples confirm that above 350 psi, coal holds about twice as much CO_2 as CH_4 and about twice as much CH_4 as N_2 (Pashin et al., 2003). The sorption capacity of coal decreases with increasing temperature (Jüntgen and Karweil, 1966; Yang and Saunders, 1985; Scott, 2002). In the Black Warrior basin, sorption capacity at a given pressure can be expected to change by about 30 percent over the range of reservoir temperatures (75-140°F; Pashin and McIntyre, this volume).

Mineral matter and moisture have minimal surface area compared to the microporous organic constituents of coal (Gan et al., 1972; Clarkson and Bustin, 1996). Accordingly, the adsorption capacity of coal is expected to decrease proportionally with increasing ash and moisture content. Pore volume also increases with increasing rank (i.e., decreasing volatile matter) (Gan et al., 1972; Clarkson and Bustin, 1997; Bustin and Clarkson, 1998), so rank parameters should correlate significantly with sorption capacity. Although results from the Black Warrior basin follow the expected rank-sorption capacity relationship (fig. 10), the positive correlation between ash content and gas sorption is counterintuitive (fig. 7). Isolating data between 5 and 21 percent ash yields the expected negative correlation (fig. 8), but coal with extremely low ash content (< 5 percent) nevertheless has retarded sorption potential (fig. 13).

The reasons for the poor performance of low-ash coal are unclear and may be related to a couple of factors. One possibility is that mineral matter helps provide structural support that decreases the sensitivity of the organic matrix to effective stress. Another possibility is that porosity in mineral matter provides conduits for gas to enter parts of the organic matrix that are otherwise inaccessible. Interestingly, Bustin (1997) noted a positive correlation between ash content and gas content in Australian coal, so ash-enhanced sorption may not be unique to the Black Warrior basin.

Relationships between gas sorption and other coal quality parameters also may not be straightforward. In a comparison of dried and moisture-equilibrated coal of bituminous rank, for example, Joubert et al. (1973, 1974) found that moisture content suppresses sorption capacity far more than would be expected on the basis of weight percentages or volumetrics. Their finding confirms that isotherms should be run on moisture-equilibrated coal to accurately characterize gas sorption under reservoir conditions. Regardless, these types of findings demonstrate that basic relationships between sorption capacity and coal quality need to be derived empirically rather than by relying on simple volumetric relationships.

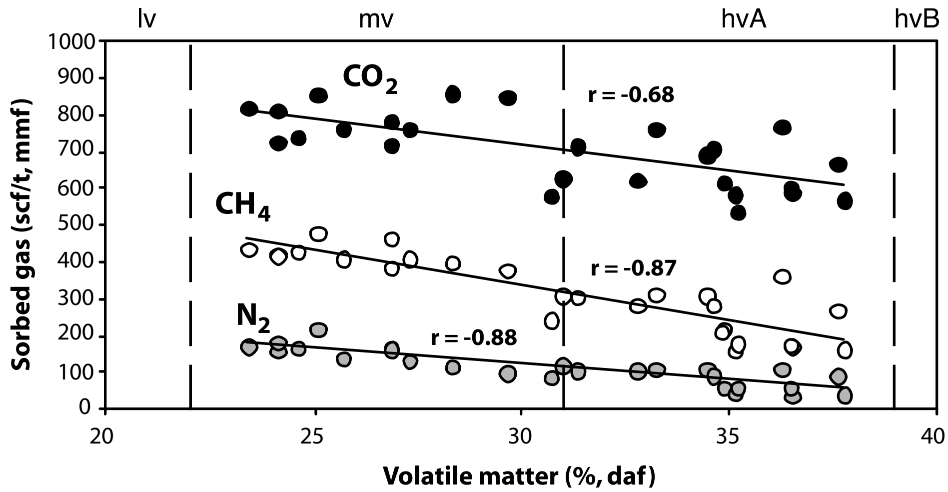

Figure 10. Correlation between rank and sorption capacity in coal of the Black Warrior basin.

In mature coalbed methane reservoirs, which have been dewatered for several years, hydrostatic pressure can be depleted to 50 psi or lower. Isotherms indicate that Pottsville coal can hold an average of 80 scf/t of CH_4 at 50 psi and 128 scf/t at 100 psi (fig. 2), so a significant gas resource appears to remain untapped. At these same pressures, coal can hold an average of 230 to 360 scf/t of CO_2, so large volumes of CO_2 may be required to fully saturate coal and recover all of the remaining coalbed methane. By contrast, coal typically adsorbs only about 18 to 33 scf/t of N_2 at these pressures, so relatively little N_2 may be required for enhanced coalbed methane recovery.

Little research has been done on the sorption selectivity of coal relative to these three gases, but experiments in the San Juan basin suggest that N_2 breaks through early, whereas early breakthrough of CO_2 has not been observed (Stevens et al., 1999a, b). This research further indicates that coal does not need to be fully saturated with CO_2 to drive enhanced coalbed methane recovery. Perhaps an optimal mix of CO_2 and N_2 is attainable that provides for efficient enhanced coalbed methane recovery while minimizing the cost of refining CO_2 derived from power-plant flue gas streams.

Summary and Conlcusions

Coal quality has a significant impact on the gas sorption capacity of coal in the Black Warrior basin, and isotherms indicate that the sorption performance of coal for a given gas can vary by a factor of two. Maceral composition has a limited impact on the sorption potential of coal, although a very weak correlation was found between gas capacity and the percentage of telovitrinite. Ash content and rank, by comparison, strongly influence sorption capacity. In samples with ash content greater than 5%, ash content and sorption capacity are negatively correlated. However, the sorption potential of coal with less than 5% ash is unexpectedly low. Rank is the strongest determinant of sorption capacity in the Black Warrior basin, although CO_2 content is significantly less sensitive to rank than are CH_4 and N_2 content.

Local variation of ash content far exceeds any regional trends, whereas rank is a regionalized variable that can be interpolated between control points with some degree of confidence. Therefore, existing rank maps can be incorporated readily into estimates of sequestration potential, whereas extreme local variation of ash content is a source of error that necessitates assessment using mean values.

Sorption isotherms indicate that a significant coalbed methane resource (>80 scf/t) remains untapped in the Black Warrior basin and that large volumes of CO_2 (>230 scf/t) may be required to saturate coal and recover all the remaining gas. By comparison, relatively little N_2 is required to saturate coal, so an optimal mix of CO_2 and N_2 may be required to drive enhanced coalbed methane recovery efficiently while controlling costs.

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