ANALYSIS OF DEVONIAN BLACK SHALES IN KENTUCKY FOR POTENTIAL CARBON DIOXIDE SEQUESTRATION AND ENHANCED NATURAL GAS PRODUCTION

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Brandon C. Nuttall

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Kentucky Geological Survey
228 Mining and Mineral Resources Building
University of Kentucky
Lexington, Kentucky 40506-0107
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Abstract

Devonian gas shales underlie approximately two-thirds of Kentucky. In the shale, natural gas is adsorbed on clay and kerogen surfaces. This is analogous to methane storage in coal beds, where CO$_2$ is preferentially adsorbed, displacing methane. Black shales may similarly desorb methane in the presence of CO$_2$.

Drill cuttings from the Kentucky Geological Survey Well Sample and Core Library are being sampled to collect CO$_2$ adsorption isotherms. Sidewall core samples have been acquired to investigate CO$_2$ displacement of methane. An elemental capture spectroscopy log has been acquired to investigate possible correlations between adsorption capacity and mineralogy.

Average random vitrinite reflectance data range from 0.78 to 1.59 (upper oil to wet gas and condensate hydrocarbon maturity range). Total organic content determined from acid-washed samples ranges from 0.69 to 4.62 percent. CO$_2$ adsorption capacities at 400 psi range from a low of 19 scf/ton in less organic-rich zones to more than 86 scf/ton in the Lower Huron Member of the shale.

Initial estimates based on these data indicate a sequestration capacity of 5.3 billion tons of CO$_2$ in the Lower Huron Member of the Ohio Shale of eastern Kentucky and as much as 28 billion tons total in the deeper and thicker parts of the Devonian shales in Kentucky. Should the black shales of Kentucky prove to be a viable geologic sink for CO$_2$, their extensive occurrence in Paleozoic basins across North America would make them an attractive regional target for economic CO$_2$ storage and enhanced natural gas production.
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Executive Summary

Increased emissions of CO\textsubscript{2}, especially from the combustion of fossil fuels, are being linked to global climate change and are of considerable global concern. These concerns are driving initiatives to develop carbon management technologies, including geologic sequestration of CO\textsubscript{2}. One option for sequestration may be Devonian black shales, organic-rich rocks that serve as both the source and trap for natural gas. Most of the natural gas is adsorbed on clay and kerogen surfaces, very similar to the way methane is stored within coal beds. It has been demonstrated in gassy coals that, on average, CO\textsubscript{2} is preferentially adsorbed, displacing methane at a ratio of two for one. Black shales may similarly desorb methane in the presence of adsorbing CO\textsubscript{2}. If this is the case, black shales may be an excellent sink for CO\textsubscript{2} and have the added benefit of serving to enhance natural-gas production. A bibliography of Devonian shale has been compiled to identify previous work and provide supporting data for continued research.

Because of the volume of material lost during washing the sampling protocol has been modified to collect cuttings before washing. Unwashed candidate samples have been selected and are being prepared for total organic carbon, vitrinite reflectance, and petrographic and CO\textsubscript{2} adsorption analyses to determine the gas-storage potential of the shale and to identify shale facies with the most sequestration potential. For the Devonian shale, average total organic carbon is 3.71 (as received) and mean random vitrinite reflectance is 1.16.

Columbia Natural Resources has provided access to a selected drill hole of opportunity for collecting sidewall cores and an advanced logging suite for correlation and mineralogical analysis. Sidewall cores have been submitted for methane and CO\textsubscript{2} adsorption isotherms and methane displacement analyses.

The final sample sets were submitted for analysis. These samples included New Albany Shale (Illinois Basin) and the Battelle deep well in Mason County, West Virginia (AEP #1) to obtain both methane and CO\textsubscript{2} adsorption isotherms. No new adsorption isotherms were completed during this quarter. Initial x-ray diffraction analyses to assist in mineral characterization and correlating results from electron capture spectroscopy logging.

Measured CO\textsubscript{2} adsorption capacity ranges from 37 to 2,078 standard cubic feet CO\textsubscript{2} per ton of shale. The values representing the higher end of this range are problematic and the samples are being re-processed. Initial estimates at 68 scf/ton indicate a sequestration capacity of 5.3 billion tons CO\textsubscript{2} in the Lower Huron Member of the Ohio shale in parts of eastern Kentucky. At 500 psia, adsorption capacity of the Lower Huron Member of the shale averages 72 scf/ton. Assuming a thickness weighted average adsorption capacity of 40 scf/ton, as much as 28 billion tons total in the deeper and thicker portions of the Devonian shales in Kentucky. The black shales of Kentucky could be a viable geologic sink for CO\textsubscript{2}, and their extensive occurrence in Paleozoic basins across North America would make them an attractive regional target for economic CO\textsubscript{2} storage and enhanced natural gas production.
Technology Transfer Summary

- NE/SE Combined GSA Section Meeting, April 2-5, 2002, Lexington, KY
- 2nd National Conference on Carbon Sequestration (NETL), May 5-8, 2003, Alexandria, VA: (poster session)
- Kentucky Oil and Gas Association Annual Meeting, June 23-25, 2003, Louisville, KY
- 2003 GSA Annual Meeting and Exposition, November 2-5, 2003, Seattle, WA
- DOE/NETL Carbon Sequestration Project Review, March 29 to April 1, 2004, Pittsburgh, PA
- AAPG Annual Meeting, April 18-21, 2004, Dallas, TX.
- 3rd Annual Conference on Carbon Sequestration (NETL), May 2-6, 2004, Alexandria, VA.
- 7th International Conference on Greenhouse Gas Control Technologies, September 5-9, 2004, Vancouver, BC, Canada: (upcoming poster session, abstract accepted)
- AAPG Eastern Section, October 3-7, 2004, Columbus, OH: (upcoming, abstract accepted)
- 2004 GSA Annual Meeting and Exposition, November 7-10, Denver, CO: (upcoming, abstract accepted)

Introduction

Carbon dioxide (CO₂) is an efficient heat-trapping gas occurring in Earth's atmosphere. Over the past decades, there has been a growing concern that anthropogenic emissions of CO₂ are contributing to a systematic warming of Earth's climate; that is, global warming. The majority of anthropogenic emissions of CO₂ are from fossil fuel combustion. Electric power generation, transportation fuels, and industrial applications are highly dependent on coal, crude oil, and natural gas. It is estimated that the reliance on fossil fuel combustion will extend well into the 21st century (EIA, 2000). In Kentucky, 95 percent of the total electric generation capacity relies on fossil fuels (EIA, 2002, Table 4), with annual emissions of 87 million metric tonnes of CO₂ (EIA, 2002, Table 7).

CO₂ emissions can be decreased by increasing the efficiency of fossil fuel combustion processes, switching to alternate and renewable fuels (biomass, nuclear, solar, wind), and capturing and sequestering CO₂. Each of these methods will undoubtedly be used to achieve goals for addressing global warming and meet increasing energy demands. For sequestering CO₂, marine and terrestrial options are being researched, but geologic sequestration is the focus of this project. Geologic sequestration includes long-term carbon storage in old oil and gas fields, coals, saline aquifers, and unconventional reservoirs.

Usually considered to be the seal for conventional oil and gas reservoirs, gas shales warrant study as a possible sequestration option. This research tests the hypothesis that organic- and gas-rich black shales can adsorb significant amounts of CO₂. In carrying out the research, the Devonian black shales of Kentucky are being tested in the laboratory to determine their CO₂ sorption capacity using powdered drill cuttings. The ability of sorbed CO₂ to displace methane is being tested on sidewall cores in order to assess the potential for enhanced natural gas production from the shales.

Organic matter in the Devonian gas shales has large surface areas similar to that found in coal. Coal seams are currently being investigated as potential sequestering sites for CO₂, the most important greenhouse gas (IEA Coal Research, 1999). Naturally occurring organic matter (kerogen) is a microporous material that possesses a very high surface area and hence sorption capacity for gas. In the subsurface, coal commonly has economically significant amounts of sorbed methane (coalbed methane). Because organic matter has a greater sorption affinity for CO₂ than methane, injection of CO₂ with simultaneous production of methane may be viable (see Reznik and others, 1982; Bachu and Gunter, 1998). Currently a pilot CO₂ injection project...
is under way in Alberta, led by the Alberta Research Council and a consortium of petroleum companies. In the San Juan Basin, New Mexico, Amoco has carried out a pilot investigation of CO$_2$ injection, and Burlington Resources is currently evaluating the utility of CO$_2$ injection to enhance recovery of methane from coal. Results from these tests have shown that CO$_2$ injection and co-production of coalbed methane is technically and economically feasible. Since 1996, over 57 million m$^3$ of CO$_2$ has been sequestered in Cretaceous coal of the San Juan Basin, New Mexico. The question is: can Devonian gas shales adsorb sufficient amounts of CO$_2$, making them significant targets for CO$_2$ sequestration?

Study Area

The study area is primarily confined to the major gas-producing area of the Ohio Shale in the Big Sandy Gas Field, eastern Kentucky (Figure 1, main concentration of producing localities). As key wells and available samples are identified, wells in deep (at least 1,000 feet) and thick (at least 50 feet) areas will be included. Two Illinois Basin wells have also been sampled. Battelle has contributed drill cuttings through the Devonian shale from their deep AEP CO$_2$ sequestration project well in Mason County, W. Va.

Regional Geology

Thinly bedded, fissile shales of Early Mississippian and Late Devonian age occur in the subsurface of nearly two-thirds of Kentucky. In general, the shales are thicker and deeper in eastern and western Kentucky (Figure 1) and are absent in the Bluegrass Region of central Kentucky and the Mississippi Embayment Region in the Jackson Purchase area of extreme western Kentucky. Along the axis of the Cincinnati Arch in central Kentucky, the thickness of the shale is usually 50 feet or less. The shale thickens eastward to more than 1,700 feet in Pike County. The shale is exposed in outcrop around the margin of the Jessamine Dome (along the perimeter of the Inner and Outer Bluegrass Regions of central Kentucky) and along the Cumberland River drainage in south-central Kentucky. A subcrop of the shale has been identified beneath the Cretaceous sediments of the Mississippi Embayment Region of western Kentucky. Figure 2 shows the elevation of the top of the Devonian shale in Kentucky and illustrates the progressive deepening of the shale east and west of the Cincinnati Arch area of central Kentucky.

Stratigraphy

Figure 3 shows the distribution of the Devonian shales in Kentucky, known variously as the New Albany (Illinois Basin), Chattanooga (central Kentucky, Cincinnati Arch area), and Ohio (Appalachian Basin) Shales. Reservoir integrity for CO$_2$ sequestration is a concern. Figure 4 provides a composite general geologic column illustrating more than 3,800 feet of Mississippian and Pennsylvanian lithologies, including carbonate, sand, shale, and coal that have proven an effective seal for existing shale gas resources. The assumption that sequestration will take place in the shale at depths of at least 1,000 feet recognizes the possible limitations of a fractured reservoir to act as an effective seal. Testing the integrity of this seal with respect to CO$_2$ is beyond the scope of this project and will be the subject of any subsequent CO$_2$ injection demonstration project.

The Ohio Shale is subdivided into seven recognizable units (Figure 5): Cleveland Shale, Three Lick Bed, Upper, Middle, and Lower Huron, Olentangy, and Rhinestreet. The Olentangy and Rhinestreet black shales correspond to the Java Formation of West Virginia, and thin and pinch out westward. Some authors consider that the Olentangy and Rhinestreet are members of the Devonian Ohio Shale. Although they are not everywhere present in the subsurface in the study area, the units are included in the analyses where samples are available.
**Production**

The first Devonian shale gas wells were drilled between 1863 and 1865 in Meade County, west-central Kentucky, and were used to fuel street lamps and provide heat in Louisville. Shale gas was discovered in eastern Kentucky circa 1892 in Floyd County (Hoeing, 1905). Overall, cumulative Devonian shale gas production in Kentucky probably exceeds 84.9 billion cubic meters (bm$^3$); gas in place is estimated by various investigators to be between 26 trillion cubic meters (tm$^3$) and 73 tm$^3$ (Hamilton-Smith, 1993, p. 5). According to production data on file at the Kentucky Geological Survey, the giant Big Sandy Gas Field of Floyd, Knott, Letcher, Martin, and Pike Counties produced 77 percent of the nearly 2.5 bm$^3$ of natural gas produced in Kentucky in 2002.

Reservoir parameters for the Big Sandy Gas Field were summarized in the "Atlas of Major Appalachian Gas Plays" (Boswell, 1996). The average completed interval exceeds 500 feet in thickness. Average porosity is 4.3 percent, with a maximum of 11 percent. Reservoir temperature averages 84°F, with an initial reservoir pressure of 800 psi or more. Current reservoir pressure averages 400 psi. Limited permeability data are available, but indicate less than 0.1 milidarcy of matrix permeability. Fracture permeability may exceed several hundred millidarcies.

Drilling and completions target organic-rich intervals with abundant natural fractures, mostly in the Lower Huron Member of the Ohio Shale (Figure 5) of eastern Kentucky. Nitrogen is typically used as the carrier fluid in hydraulic fracturing stimulations, which are intended to intersect with and enhance any natural fractures. Sand is generally employed as a proppant to maintain an open fracture system. The industry rule of thumb is that a shale well can be expected to produce 300 million cubic feet of natural gas (MMcf). Some wells often produce from 500 MMcf to more than 1 billion cubic feet. Devonian shale gas production tends to be long-term. This long-term production (with many wells exhibiting flat, or inclining production; see Figure 6) and high organic content suggest the shale contains a large component of adsorbed methane.

**Methods**

**Drill Cuttings**

Drill cuttings on file at the Kentucky Geological Survey Well Sample and Core Library and sidewall cores are the main source of material for analysis. Unwashed sets of recently acquired drill cuttings were used to minimize weathering of material and to maximize volume of material for analysis. Drill cuttings are commonly collected during drilling in 5- to 10-foot intervals and consist of a mix of chipped rock fragments and powder. Distribution and stratigraphy of the Devonian shale in eastern Kentucky suggest dividing well cuttings into up to three samples for adsorption analysis. The upper part of the shale from the Cleveland Member to the Middle Huron is generally less organic-rich, as indicated by the gamma-ray response on standard geophysical well logs (Figure 5). Drill cuttings of this sequence generally have a lighter gray color and more recognizable quartz material than the darker gray to black samples with sparse pyrite that are characteristic of the Lower Huron Member. In some areas of the Big Sandy Gas Field, the Olentangy and Rhinestreet Members of the Ohio Shale are present but have a somewhat lesser organic content as indicated by gamma-ray logs. Where present, these shales were composited as a separate sample. Some wells have an insufficient volume of cuttings available to analyze the individual members of the Ohio Shale; in these cases the entire shale sequence was composited into a single sample. The rock chip and powder samples were divided into two splits: one for TOC, vitrinite reflectance, and X-ray diffraction analyses, and one for determination of CO$_2$ isotherms. Each split was then milled and sieved to the specifications...
of the respective analytical technique. Figure 7 shows the location of wells sampled to date in eastern Kentucky.

**Total Organic Carbon**

To investigate any relation between organic content and CO$_2$ sorption capacity, total organic carbon content (TOC) is being determined. For total organic carbon analyses, samples were first crushed to a maximum particle size of 200 microns (–60 mesh). Samples were run in duplicate. One split was run “as is.” Another split was treated with 30 percent hydrochloric acid (HCl) for 12 to 24 hours to remove any carbonate minerals from the matrix, prior to analysis. Although carbonate minerals are typically a rare component of Devonian shales, they present a possible bias in the calculation of TOC. Like organic material, carbonate minerals dissociate in the combustion chamber and form CO$_2$. The hydrochloric acid was removed by repeated washings with distilled water, followed by centrifugation. The samples were then placed in a drying oven (50°C).

Total organic carbon was measured on a LECO SC-144 DR dual range sulfur and carbon analyzer, which is a nondispersive, infrared, digitally controlled instrument designed to measure sulfur and carbon in a wide variety of organic and inorganic materials. The unit combusts samples in a pure oxygen environment at 1,350°C. Sulfur compounds are immediately oxidized and form sulfur dioxide (SO$_2$); carbon compounds are oxidized to CO$_2$. From the combustion system, sample gases pass through two tubes containing magnesium perchlorate (MgClO$_4$), which removes moisture, and then are routed to the infrared (IR) detection cells. A sulfur IR cell measures the amount of SO$_2$ present in the gas stream, and a carbon IR cell does the same for CO$_2$. All molecules, with the exception of bipolar species (e.g., N$_2$, H$_2$, O$_2$), absorb energy in the infrared region. As radiant energy is projected through the sample material an IR absorption spectrum is produced. Since no two molecules produce the same spectrum, the identity and quantity of a compound can be readily, and accurately, determined.

**Vitrinite Reflectance**

Vitrinite reflectance is used as a measure of the maturity of the organic matter in shale and that maturity may influence CO$_2$ sorption capacity. Mean random reflectance ($R_{\text{random}}$) on dispersed vitrinite particles in the samples was determined on a Zeiss USMP incident light microscope calibrated using glass standards of known reflectance. Depending on the amount of vitrinite in the samples, 50 or 100 grains were measured at a magnification of 640x to determine mean reflectance. Mean random reflectance was used because it eliminates the need to rotate the stage to determine maximum and minimum reflectance values. As the vitrinite particles in the analyzed samples were quite small (usually less than 10 microns), stage rotation simply wasn’t practical, because it often resulted in the reflectance measuring spot moving off the grain. Maximum vitrinite reflectance values ($R_{\text{max}}$) can be estimated by multiplying the mean random measurements by 1.066 (Ting, 1978).

**Adsorption Isotherms**

The classic theory used to describe the type I isotherm for microporous materials with small external surface area is based on the Langmuir equation (1916). The type I isotherm displays a steep increase in adsorption at low relative pressures due to enhanced adsorption caused by the overlapping adsorption potentials between the walls of pores whose diameters are commensurate in size with the adsorbate molecule. The type I isotherm then flattens out into a plateau region at higher relative pressure, which is believed to be caused by the completion of a monolayer of adsorbed gas. The micropore volume is thought to then be filled
by only a few molecular layers of adsorbate, and further uptake is limited by the dimensions of the micropores.

The Langmuir model assumes that a state of dynamic equilibrium is established between the adsorbate vapor and the adsorbent surface and that adsorption is restricted to a single monolayer. The adsorbent surface is thought to be composed of a regular array of energetically homogeneous adsorption sites upon which an adsorbed monolayer is assumed to form. The rate of condensation is assumed to be equal to the rate of evaporation from the adsorbed monolayer at a given relative pressure and constant temperature. The Langmuir equation was developed with these assumptions and takes the following form:

\[
\frac{P}{V} = \frac{1}{BV_m} + \frac{P}{V_m}
\]

where \( P \) is the equilibrium pressure, \( V \) is the volume of gas adsorbed at equilibrium, \( V_m \) is the volume of adsorbate occupying the monolayer, and \( B \) is an empirical constant. A plot of \( P/V \) vs. relative pressure should yield a straight line whose slope will yield \( V_m \), from which the surface area may be obtained.

The Langmuir isotherm can be written:

\[
V(P) = \frac{V_L P}{P_L + P}
\]

\( P \) = gas pressure
\( V(P) \) = predicted amount of gas adsorbed at \( P \)
\( V_L \) = Langmuir volume parameter
\( P_L \) = Langmuir pressure parameter

The difference between the measured amount of gas adsorbed (\( V(P) \)) and that predicted using the Langmuir equation (\( V_i(P) \)) is a measure of error and is given as:

\[
Err(P) = V_i(P) - V(P)
\]

This error may be positive or negative. The square of the error is always positive and is a measure of how well the calculated isotherm matches the data. This error can be calculated for each point and summed giving a measure of the overall error:

\[
SSE = \sum_{i=1}^{N} Err_i^2
\]

\( N \) = number of measured points

The goodness of fit of the isotherm is expressed by calculating the correlation coefficient between the measured points and the calculated points. The results generally yield correlations that are better than \( r^2 = 0.99 \), and standard errors of Langmuir volumes of \( \pm 2 \) percent. The reported CO\(_2\) sorption capacity and corresponding pressure are calculated coefficients of the Langmuir model and are used to determine the sorption capacity at reservoir-appropriate pressures (Table 2).
Adsorption analyses were performed using a high-pressure volumetric adsorption technique similar to that described by Mavor and others (1990). Isotherms were measured on a custom-made apparatus modeled after a similar module designed and built at CSIRO in Lucas Heights, Australia. The apparatus is based on Boyle’s Law. In simple terms, a known volume of gas within a reference cell is used to dose a sample cell that contains the sample. The amount of gas adsorbed in the sample cell is then determined, based on a change in pressure in the sample cell using the Real Gas Law. Following dosing of the sample cell, the pressure drops until equilibrium is reached (i.e., no more gas can be adsorbed by a sample at a particular pressure). When equilibrium is reached, the sample is dosed at a higher pressure. Typically, 11 separate pressure points are selected and measured so that a Langmuir regression curve can be accurately generated. The pressures in the reference and sample cells are measured using pressure transducers that are interfaced to a computer equipped with special boards and software. The computer monitors the transducers and determines when equilibrium is reached; it also controls valves and switches for dosing and purging the cells.

**Sidewall Cores for Adsorption and Methane Displacement**

Laboratory investigation of methane displacement in the presence of CO$_2$ is being performed on whole rock core samples. In cooperation with Columbia Natural Resources, access to a well in Knott County, eastern Kentucky, was obtained for logging and collection of sidewall cores. Schlumberger Oilfield Services provided elemental capture spectroscopy logging for mineral identification and obtained the sidewall cores. The sidewall core plugs are being saturated with methane. To test the potential for enhanced natural gas production, the cores are being subjected to simulated injection of CO$_2$, and the amount of methane displaced during injection is being measured. Laboratory setup and analyses are similar to the standard procedure for obtaining adsorption isotherms.

**Mineralogy: Elemental Capture Spectroscopy and X-Ray Diffraction**

Elemental capture spectroscopy (ECS) is an advanced tool used for lithology and mineral determination that uses the same technology employed by NASA on the Mars Rover missions. An AmBe neutron source is used to activate a formation. Relative elemental yields are derived using fourier transform infrared spectroscopy analysis to identify 23 elements. Primary elements measured include: Si, Ca, Fe, S, Ti, Gd, Cl, and H. The relative abundance of these elements has been correlated with particular minerals and sedimentary lithologies (Herron and Herron, 1997 and Schlumberger, 2000). To supplement the ECS log, x-ray diffraction (XRD) data are being acquired. Samples for XRD analysis are pulverized to 200 mesh or smaller and side packed.

**Sequestration Capacity of the Shale**

ArcView GIS software was used to develop a method to compile an estimate of the sequestration capacity of the shale. The method uses a cell-based approach that enables combining shale thickness and depth information in the form of continuous grids with shale density and spatially variable CO$_2$ adsorption capacity data. Preliminary estimates were compiled using a uniform, minimum CO$_2$ adsorption capacity and include data projected into the Illinois Basin portion of western Kentucky.
Results to Date

Thirty-three samples have been collected from 11 wells, including three cuttings samples and 10 sidewall cores from the Columbia Natural Resources No. 24752 Elkhorn Coal Corporation well in Knott County (Figure 8). Data for completed analyses are presented in Table 1. In recognition of the regional nature of the potential reservoir, both the Midwest Geologic Sequestration Consortium (Illinois Basin, ISGS) and the Midwest Regional Carbon Sequestration Partnership (Appalachian Basin, Battelle) were contacted to obtain shale samples. Illinois Basin core samples and drill cuttings from the Battelle AEP test well have been acquired and submitted for analysis.

$R_0^{\text{random}}$ values (Table 1) range from a minimum of 0.78 to 1.59 with a median of 1.1 and a mean of 1.2. This places the shale in the upper oil to wet gas and condensate maturity range as measured by reflectance. In Figure 9. Mean random reflectance ($R_0^{\text{random}}$), axis labels refer to the upper (right) end of the graphed class.

The currently available adsorption isotherms are presented in Figure 10. The Langmuir volume and pressure data reported in Table 1 must be compared on a uniform pressure basis by formation. These summary data are shown in Table 2 which shows calculated adsorption capacities at three pressure values that are expected to be typical of the range of observed Devonian shale gas reservoir conditions. To effectively compare capacity data derived from adsorption isotherms, three pressure conditions were selected: 300, 400, and 500 psia. These comparison data are presented in Figure 11.

Columbia Natural Resources (CNR, now owned by Triana) drills a number of Devonian shale gas wells in eastern Kentucky as a normal part of their resource development program. A drill hole of opportunity was identified and sidewall cores and logs were obtained from the well. An elemental capture spectroscopy (ECS) log was obtained. The cores have been submitted for laboratory analysis by saturation with CH$_4$ and analysis of CH$_4$ displacement efficiency as CO$_2$ is injected into the core. The CNR well number 24752 Elk Horn Coal Company is located in eastern Knott County (Figure 8).

The ECS log presents dry weight fractions of major lithologic components including silicates (quartz, feldspar, and mica), clay minerals, and carbonates. Figure 12 shows a portion of the ECS log through the Lower Huron Member of the Devonian Ohio Shale in the CNR well 24725 Elk Horn Coal. As measured on the ECS log through the complete Ohio Shale interval, the dry weight fraction of clay ranges from a minimum of 25 percent to a maximum of 71 percent. The mean clay content is 55 percent and the mode is 63 percent. Figure 13 shows a typical whole rock x-ray diffraction trace indicating the presence of Illite, Kaolinite, Pyrite, and Quartz. Another clay mineral (indicated by “M” in the figure) is most likely an authigenic Smectite (possibly Montmorillonite). Hosterman and Whitlow (1983) reported an Illite-Smectite mixed layer clay (consistent with Montmorillonite). Selected samples are being re-analyzed at higher resolution to better resolve the peak positions for identification.

Ten sidewall cores were recovered and are summarized in Appendix C. Of these cores, 7 were intact and have been submitted for CO$_2$ adsorption and methane displacement analysis. The three broken cores are being analyzed for solvent extraction for chromatographic analysis to identify any light hydrocarbons present and for petrographic analysis. Appendix C also includes sections of the litho-density and elemental capture spectroscopy logs acquired.

Initial estimates of CO$_2$ sequestration capacity have been calculated using selected data. An initial estimate of the sequestration volume of the Lower Huron was compiled using areal distribution and thickness data from Dillman and Ettensohn (1980). Initial calculations indicate that 91 x $10^{12}$ cubic feet ($2.6 x 10^{12}$ cubic meters) of CO$_2$ could be sequestered in the Lower Huron using a Langmuir volume of 67.6 scf/ton (2.1 m$^3$/tonne; raw data from sample 107928-2 (Table 1) and an average thickness of 150 feet over the area of Boyd, Breathitt, Floyd, Johnson,
Knott, Lawrence, Leslie, Magoffin, Martin, Perry, and Pike Counties combined. Assuming 30 percent of this theoretical saturation, approximately 1.6 billion tons (1.5 billion metric tonnes) of CO₂ could be sequestered. Using a 1-kilometer grid, a depth to top of shale of 1,000 feet or greater, a shale thickness of 50 feet or more, and a constant adsorption capacity equal to a thickness-weighted average of 40 scf/ton (1.2 m³/tonne; raw data from samples 107928-1, 107928-2, and 107928-3, Table 1), estimated initial CO₂ sequestration capacity of the Devonian shale in Kentucky is 27.7 billion tons (25.1 billion metric tonnes) (Figure 14).

Preliminary Conclusions

Preliminary data indicate that black, organic-rich gas shales can serve as targets for sequestration of significant volumes of anthropogenic CO₂. At Kentucky's current rate of power plant emissions, the organic-rich, black shale in the state could sequester more than 300 years' worth of that carbon. Enhanced production of natural gas displaced by the injected CO₂ would contribute to a long-term increase in the supply of what is considered a "greener" fuel.

Acknowledgements

The authors want to thank the University of Kentucky Research Foundation and the Office of Sponsored Projects Administration for their assistance and support. Ed Rothman of Columbia Natural Resources (Triana) and Jay Terry of Schlumberger were instrumental in providing access to a drill hole and obtaining advanced well logs. Henry Francis, Laboratory Services Manager, is conducting x-ray diffraction analyses. Dr. Sue Rimmer, Associate Professor, Department of Geological Sciences, University of Kentucky, has assisted with analysis and interpretation of the x-ray diffraction data. Jackie Silvers of the Kentucky Geological Survey kept our budget straight and Leah Barth spent many dusty hours sampling well cuttings.
References Cited


# Tables

**Table 1.** Gas storage capacity, total carbon (TC), total organic carbon (TOC), and vitrinite reflectance data for completed samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Formation</th>
<th>Reported (\text{CO}_2) scf/ton</th>
<th>(\text{CO}_2) psia</th>
<th>TC as rec’d</th>
<th>TOC (acid*)</th>
<th>(R_0)random</th>
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<td>107928-1</td>
<td>Upper Ohio</td>
<td>37.5</td>
<td>681.1</td>
<td>3.94</td>
<td>0.69</td>
<td>1.55</td>
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<td>107928-2</td>
<td>Lower Huron</td>
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<td>243.7</td>
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<td>121774-1</td>
<td>Ohio Shale</td>
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* Samples washed in HCl to remove carbonate (inorganic carbon)  
Scf/ton = standard cubic feet per ton  
psia = pressure, pounds per square inch absolute

**Table 2.** Summary of \(\text{CO}_2\) adsorption capacity in standard cubic feet per ton at selected pressures.

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<td>Overall</td>
<td>31.1</td>
<td>38.4</td>
<td>44.8</td>
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Figures

Figure 1. Distribution of the Devonian shale in Kentucky, showing the occurrence of deeper and thicker shale with possibly greater potential for geologic sequestration of CO$_2$.

Figure 2. General structure of the Devonian shale, showing presence of shale in the subsurface (shading).
Figure 3. Distribution and nomenclature of Devonian shales of Kentucky (Hamilton-Smith, 1993, p. 3).
Figure 4. General geologic column showing approximately 3,800 feet of overlying Mississippian and Pennsylvanian lithologies adequate for ensuring reservoir integrity in the Devonian shale. Note: Devonian shale is underlain by Devonian carbonates.
Figure 5. Nomenclature of Mississippian and Devonian shales of eastern Kentucky and key to names and codes used for intervals sampled.
Figure 6. Eastern Kentucky Devonian shale natural-gas production (proprietary data), showing long-term increase. Dotted line is exponential best fit of observed rate-time data.
Figure 7. Location of wells in eastern Kentucky sampled to date. Includes the CNR 24752 Elk Horn Coal well (125651) with ECS log, sidewall cores, and drill cuttings. Small dots are existing gas wells in region.
Figure 8. Location of the Columbia Natural Resources 24752 Elk Horn Coal Company well, permit 94539, Knott County, Ky., Carter coordinate 11-K-81, latitude 37.37019° N, longitude 82.76441° W (NAD 1983).
Figure 9. Mean random reflectance ($R_0_{\text{random}}$)
Figure 10. Summary of adsorption isotherms by formation.
Figure 11. Average calculated adsorption capacities by formation at selected pressures.
Figure 12. Section of elemental capture spectroscopy log through the Lower Huron section of the Columbia Natural Resources No. 24752 Elk Horn Coal well, Knott County, Ky., showing relative abundance of species related to mineral and lithologic identification. Asterisks denote depths where sidewall cores were recovered.
Figure 13. Typical whole rock X-ray diffraction trace of the Devonian shale (upper part, well id 107928, Figure 7).
Figure 14. Preliminary estimated CO$_2$ storage capacity per square kilometer (in million tons) in the areas of deeper (>=1,000 feet) and thicker (>=50 feet) Devonian shale.
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Appendix A: Summary of Adsorption Isotherms
**SUMMARY OF ADSORPTION ANALYSES IMP. UNITS**

Isotherm Temperature: 86.0 ºF

Goodness of fit of Langmuir regression: 0.88

Density g/cc: 2.756

### Pressure (PSIA) vs. CO₂ Adsorbed (SCF/ton)

<table>
<thead>
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<th>Adsorbed gas (ft³/ton)</th>
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### Langmuir Parameters

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107928-2 4400-4600 ft. Lower Huron Member

**SUMMARY OF ADSORPTION ANALYSES IMP. UNITS**

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<th>Adsorbed gas (ft$^3$/ton)</th>
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**Langmuir Parameters**

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<td>Pressure (PSIA)</td>
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Isotherm Temperature: 86.0 °F

Goodness of fit of Langmuir regression: 0.97 Density g/cc 2.660
**SUMMARY OF ADSORPTION ANALYSES IMP. UNITS**

Isotherm Temperature: 86.0 °F

Goodness of fit of Langmuir regression: 0.98

Density g/cc: 2.749

**107928-3 4600-5000 ft. Rhinestreet and Olentangy Members**

**Langmuir Parameters**

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**Sample Cell Equilibrium Pressure (PSIA)**

**COC adsorbed (SCF/ton)**

**Graph:**

- X-axis: Sample Cell Equilibrium Pressure (PSIA)
- Y-axis: CO2 adsorbed (SCF/ton)
SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
Goodness of fit of Langmuir regression: 0.91 Density g/cc 2.550

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In-Situ Conditions (Equilibrium Moisture)

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Goodness of fit of Langmuir regression: 0.49 Density g/cc 2.597
SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
Goodness of fit of Langmuir regression: 0.04 Density g/cc 2.579

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Langmuir Parameters

<table>
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<tr>
<th>In-Situ Conditions (Equilibrium Moisture)</th>
<th>Vol. (ft³/ton)</th>
<th>Pressure (PSIA)</th>
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RN124789 S2A 2990-3110 ft.
**SUMMARY OF ADSORPTION ANALYSES IMP. UNITS**

**Isotherm Temperature:** 86.0 °F

**Goodness of fit of Langmuir regression:** 0.77 Density g/cc 2.679
**SUMMARY OF ADSORPTION ANALYSES IMP. UNITS**

Isotherm Temperature: 86.0 °F

Goodness of fit of Langmuir regression: 0.66

Density g/cc: 2.631

### Langmuir Parameters

<table>
<thead>
<tr>
<th>In-Situ Conditions (Equilibrium Moisture)</th>
<th>Adsorbed gas (ft³/ton)</th>
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<tr>
<td>Pressure (PSIA)</td>
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<tr>
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<td>593</td>
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</table>

**CO₂ adsorbed (SCF/ton)**

Sample Cell Equilibrium Pressure (PSIA)

Vol. (ft³/ton) 228.9
Pressure (PSIA) 2230.4
ISO 8103

**SUMMARY OF ADSORPTION ANALYSES IMP. UNITS**

**Isotherm Temperature:** 86.0 °F

**Goodness of fit of Langmuir regression:** 0.96

**Density g/cc** 2.573

---

**Pressure (PSIA) | Adsorbed gas (ft³/ton)**
--- | ---
25 | 3.6
49 | 7.2
82 | 11.6
116 | 16.1
146 | 20.1
196 | 26.4
256 | 33.7
321 | 40.5
390 | 48.4
508 | 61.6
571 | 75.3

**Langmuir Parameters**

- **Vol. (ft³/ton)**: 309.3
- **Pressure (PSIA)**: 2106.0
121162 OHIO UPPER 3410-3810 ft.

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Langmuir Parameters

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SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 ºF
Goodness of fit of Langmuir regression: 0.79 Density g/cc 2.669
121464 OHIO Upper 3200-3300 ft,

Sample Cell Equilibrium Pressure (PSIA) vs. CO2 adsorbed (SCF/ton)

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<td>78</td>
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<td>193</td>
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<tr>
<td>250</td>
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<table>
<thead>
<tr>
<th>Vol. (ft³/ton)</th>
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<td>Pressure (PSIA)</td>
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**SUMMARY OF ADSORPTION ANALYSES IMP. UNITS**

Isotherm Temperature: 86.0 ºF

Goodness of fit of Langmuir regression: 0.82 Density g/cc 2.694
SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
Goodness of fit of Langmuir regression: 0.79 Density g/cc 2.716

**Pressure (PSIA)** | **Adsorbed gas (ft³/ton)** | **In-Situ Conditions (Equilibrium Moisture)**
---|---|---
14 | 5.6 |
33 | 10.3 |
52 | 15.0 |
99 | 29.0 |
113 | 30.6 |
159 | 41.4 |
218 | 55.5 |
289 | 71.7 |
362 | 82.1 |
476 | 101.1 |

**Langmuir Parameters**

<table>
<thead>
<tr>
<th>In-Situ Conditions (Equilibrium Moisture)</th>
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<th>Pressure (PSIA)</th>
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<tbody>
<tr>
<td>248.7</td>
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**121464 HURNL 4300-4380 ft.**

Sample Cell Equilibrium Pressure (PSIA)

CO₂ adsorbed (SCF/ton)
SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
Goodness of fit of Langmuir regression: 0.93
Density g/cc 2.730

<table>
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<tr>
<th>Pressure (PSIA)</th>
<th>Adsorbed gas (ft³/ton)</th>
<th>In-Situ Conditions (Equilibrium Moisture)</th>
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<td>27</td>
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<td>3.2</td>
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<tr>
<td>42</td>
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<td>123</td>
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Langmuir Parameters

<table>
<thead>
<tr>
<th>In-Situ Conditions (Equilibrium Moisture)</th>
<th>Vol. (ft³/ton)</th>
<th>Pressure (PSIA)</th>
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<tr>
<td></td>
<td>108.0</td>
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</table>
Appendix B: GIS Analysis of the Distribution and Estimated CO2 Storage Volume of the Devonian Shale in Kentucky

Note: Grid data sets are indicated in matrix notation using the courier type face, i.e., [grid_data]

Geographic information system (GIS) software was used to perform an analysis of the thickness and distribution of the Devonian black shale in Kentucky. The initial goal is to calculate the number of tons of shale in place by county for those areas with drilling depths to the shale of at least 1,000 feet and a shale thickness of at least 50 feet. These cutoffs were selected to ensure reservoir integrity (deeper than the expected depth of surface fracturing) and gas reservoir potential. With the number of tons of shale being determined, a series of factors to calculate the sequestration potential in tons of CO2 are derived based on measured CO2 storage capacity and shale density. For GIS, ESRI’s ArcView 3.2 and Spatial Analyst were used. The Kentucky Geological Survey uses a server running SQL-2000 for data storage. Data are accessed with tables linked to a graphic user interface implemented using Microsoft Access 97. Access queries were composed to compile point data sets consisting of the locations and values of Devonian shale stratigraphic tops and thickness. The formation tops data were maintained as drilling depth to the top of the formation rather than elevations with respect to sea level. Open database connectivity (ODBC) services are available from ArcView. The Access query results were added to the GIS as tables using the SQL Connect facility and then converted to shape files.

Sample SQL query composed with the Access GUI for compiling Devonian shale

```
SELECT dbo_well_identification.record_number AS recno,
       dbo_geographic_location.north_latitude AS lat,
       dbo_geographic_location.west_longitude AS lon,
       dbo_formation_tops.pick_fm,
       dbo_geographic_location.surface_elevation AS elev,
       dbo_formation_tops.fm_top,
       dbo_formation_tops.fm_base, [fm_base]-[fm_top] AS thick
FROM ((dbo_geographic_location INNER JOIN dbo_geographic_region ON
       dbo_geographic_region.location_index =
       dbo_geographic_location.location_index) INNER JOIN dbo_well_identification ON
       dbo_geographic_location.location_index =
       dbo_well_identification.location_index) INNER JOIN dbo_formation_tops ON
       dbo_well_identification.record_number = dbo_formation_tops.record_number
WHERE (((dbo_formation_tops.pick_fm)="341OHIO" Or
       (dbo_formation_tops.pick_fm)="341CHAT" Or
       (dbo_formation_tops.pick_fm)="341NALB") AND ((dbo_formation_tops.fm_top) Is Not Null) AND ((dbo_formation_tops.fm_base) Is Not Null) AND ([fm_base]-[fm_top])>0) AND ((dbo_formation_tops.type_of_top)="s") AND
       (dbo_geographic_location.ns_feet)>0) AND ((dbo_geographic_location.n_or_s) Is Not Null) AND ((dbo_geographic_location.ew_feet)>0) AND
       ((dbo_geographic_location.e_or_w) Is Not Null) AND ((dbo_geographic_location.carter_section)>0) AND
       ((dbo_geographic_location.carter_letter)="A") AND
       ((dbo_geographic_location.carter_number) Is Not Null));
```
stratigraphic and location point data.

Existing polygon shape files of the Kentucky counties, faults, and the subsurface distribution of the Devonian shale in Kentucky ([Subsurf]) were employed in the analysis. The shape file of the subsurface distribution of the shale was converted to a grid for use in the spatial analysis. Each cell of this grid contained a value of 1 (true) if the shale existed in the subsurface over the area of the cell. All other cells were set to null, the no data value. All grids were computed with 1,000-meter (1 kilometer) cell dimensions. Analyses were performed using the North American Datum of 1927 (NAD27) with the projection set to UTM zone 16.

Subsurface distribution of the Devonian shale (blue, shaded) with stratigraphic data points.

Subsurface distribution of the Devonian shale (blue, shaded) with stratigraphic data points for the Lower Huron Member of the shale.

For deriving drilling depth and thickness maps, grids were interpolated from point data using the inverse distance weighted (IDW) nearest neighbor method. The interpolated
data were processed to establish which grid cells fit the selection criteria of 1,000 feet or deeper drilling depths and a shale thickness of at least 50 feet.
Interpolate grid, [Depth], using drilling depth from point file
Interpolate grid, [Iso], using thickness data from point file
Map Query [Depth] >= 1000 = [Deep]
Map Query [Iso] >= 50 = [Thick]
Calculate [Deep] *[Thick] = [Temp01]
Calculate [Temp01] *[Subsurf] = [Temp02]
([Temp02] = 0.AsGrid).SetNull([Temp02]) = [DeepThick]

Method for deriving a grid dataset indicating the distribution of shale at least 50 feet thick and 1,000 feet deep.

To restrict the volume calculations to the limits of the distribution of thicker and deeper shale, the [Iso] and [DeepThick] grid data sets were multiplied together to produce a new grid, [Target].

To limit the number of calculation steps required to derive volume and sequestration potential estimates, conversion factors were derived to convert the thickness (isopach in feet) data in [Target] to million tons of shale and then directly to CO2 tons. Tons of shale in place is a function of shale volume and density, thus:

\[ Tons_{\text{shale}} = \text{volume} \times \text{density} \]

and

\[ MMTons_{\text{shale}} = \frac{\text{thickness} \times \text{area} \times \text{density}}{1000000} \]

Assuming thickness in feet, a 1 kilometer cell size, a density in g/cc million tons of shale in place can be calculated:

\[ MMTons_{\text{shale}} = \frac{\text{thickness} \times 0.3048 \text{m}}{\text{ft}} \times \left(1000\text{m}\right)^2 \times \text{density} \times 1.102 }{1000000} \]

Eq. 1.

where:
- thickness = thickness of shale in feet
- 1000 = cell size in meters
- density = bulk density from compensated density log
- 1.102 = density conversion factor to convert from grams per cubic centimeter to tons per cubic meter
For a specified density, the constants in equation 1 can be combined to obtain a direct conversion factor that is a function only of shale thickness. Substituting different shale densities, a factor, \( C_{\text{FMM Tons}} \), would be one of:

\[
\begin{align*}
2.5 \text{ g/cc (log estimated density for Lower Huron)} & = 0.840 \\
2.6 \text{ g/cc (log estimated density for upper part of shale)} & = 0.873 \\
2.65 \text{ g/cc (log handbook typical shale density)} & = 0.890
\end{align*}
\]

To calculate million tons of shale per cell, the ArcView grid calculation would be:

\[
\text{[Target]} \times C_{\text{FMM Tons}} \text{.AsGrid} = \text{[MMTons]}
\]

Different conversion factors could be derived for standard reservoir analysis (as opposed to assuming adsorbed gas). Distributions of porosity, water or oil saturation data, and others could be gridded and used to derive oil or gas in place estimates.

Converting tons of shale in place to estimated tons of CO\(_2\) sequestered requires an additional factor based on the gas content per ton of shale from CO\(_2\) adsorption data. Using a gas content of 1 standard cubic foot of CO\(_2\) per ton and 17.25\(^1\) thousand cubic feet (Mcf) CO\(_2\) per ton of CO\(_2\), there will be 57.97 tons of CO\(_2\) per million tons of shale.

\[
\frac{TonsCO_2}{ton_{\text{shale}}} = \frac{ft^3}{ft^3} \times \frac{Mcf}{1000ft^3_{CO_2}} \times \frac{ton_{CO_2}}{17.25Mcf} = 57.97
\]

Eq. 2

The sequestration volume in tons of CO\(_2\) can now be considered a function of thickness, shale density, and adsorbed gas content, or:

\[
TonsCO_2 = 57.97 \times C_{\text{FMM Tons}} \times \text{thickness} \times \text{gas content}
\]

Multiplying the 57.97 and \( C_{\text{FMM Tons}} \) provides a single factor that varies only with density:

\[
\begin{align*}
\text{Factor} & = 48.69 \text{ at density equals 2.5 g/cc} \\
\text{Factor} & = 50.61 \text{ at density equals 2.6 g/cc} \\
\text{Factor} & = 51.59 \text{ at density equals 2.65 g/cc}
\end{align*}
\]

In lieu of gridding gas content data, multiplying a measured gas content by one of these factors yields a final selection of factors for use in converting shale thickness data directly to tons of CO\(_2\) sequestered. For example, using a gas content of 40 scf/ton, a shale density of 2.6 g/cc, and a 1000-meter cell size, the tons of CO\(_2\) per cell is 2024.3 per foot of shale thickness, thus:

\[
\text{[Target]} \times (2024.3) \text{.AsGrid} = \text{[CO2Tons]}
\]

\(^1\) 17.25 Mcf CO\(_2\) per ton CO\(_2\) is the conversion factor used by the U.S. EPA. Conversion is derived from gas laws and is valid for 60°F and 1 atmosphere pressure.
As additional gas content data are acquired, examining the distribution and gridding the data as appropriate will be used to refine the sequestration volume calculations.

The values calculated for each cell require summation for specific regions to obtain totals. With the county polygon theme active, the ArcView Summarize Zones procedure (available from the Analysis menu command) was used to summarize the data by county. The field defining the zones was the county name and the [CO2Tons] grid theme was selected for summarizing. A table of summary statistics was computed that could be joined to the original county table for mapping and additional analysis.

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<th>Name</th>
<th>Basin</th>
<th>Count</th>
<th>Min</th>
<th>Max</th>
<th>Mean</th>
<th>MM Tons CO2</th>
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Years sequestration available at 80,000,000 tons CO2 per year 346.2
The values shown in this table are provided to illustrate an application of the estimation method described in this appendix. The numbers are subject to revision and do not represent final conclusions of this project. Additional CO$_2$ adsorption capacity data will be acquired to refine the estimates. Consideration will be given to other adjustments to the total that might include evaluating areas likely to have little or no sequestration potential even though they are mathematically included in the area of deep and thick shale. These areas will be excluded. For example, based on experience in oil and gas field exploration and development, Marshall, Pulaski, and Rockcastle counties are areas of marginal potential that have a relatively small likely- hood of being developed for carbon sequestration.
Appendix C: CNR 24752 Elk Horn Coal

Recno: 125651  
Permit: 94539  
Name: Columbia Natural Resources 24752 Elk Horn Coal Corp  
Loc: Knott County, KY, 1250 FSL 620 FWL 11-K-81  
Lat: 37.3701 N (NAD27)  
Lon: -82.764533 W  
TD: 3004 feet

Log measured from KB @ 1011’

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Core samples are identified by their respective measured depth from KB (i.e., Top value in **bold**).
Sidewall core number 3 (0.25-inch grid). This sample included a pyrite clast but is otherwise typical of the intact cores as submitted for analysis.

Sidewall core number 2 (0.25-inch grid). This sample exhibits an oily sheen characteristic of cores collected that were saturated with light hydrocarbons. This core is typical of the broken samples.
Annotated section of the litho-density log for the CNR 24752 Elk Horn Coal well, Knott County.
CNR 24752 Composite log suite through the (Devonian) Lower Huron showing locations of recovered cores (red arrows, right track of Litho-Density log).