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

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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 CO₂ is preferentially adsorbed, displacing methane. Black shales may similarly desorb methane in the presence of CO₂.

Drill cuttings from the Kentucky Geological Survey Well Sample and Core Library are being sampled to collect CO₂ adsorption isotherms. Sidewall core samples have been acquired to investigate CO₂ 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. CO₂ 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 CO₂ 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 CO₂, their extensive occurrence in Paleozoic basins across North America would make them an attractive regional target for economic CO₂ storage and enhanced natural gas production.

Table of Contents

DISCLAIMER	I
ABSTRACT	II
TABLE OF CONTENTS	III
LIST OF TABLES	IV
LIST OF FIGURES	IV
EXECUTIVE SUMMARY	1
TECHNOLOGY TRANSFER SUMMARY	2
INTRODUCTION	2
STUDY AREA	3
REGIONAL GEOLOGY	3
STRATIGRAPHY	3
PRODUCTION	4
METHODS	4
Drill Cuttings	4
Total Organic Carbon	5
Vitrinite Reflectance	5
Adsorption Isotherms	5
Sidewall Cores for Adsorption and Methane Displacement	7
Mineralogy: Elemental Capture Spectroscopy and X-Ray Diffraction	7
Sequestration Capacity of the Shale	7
RESULTS TO DATE	8
PRELIMINARY CONCLUSIONS	9
ACKNOWLEDGEMENTS	9
REFERENCES CITED	10
TABLES	11
FIGURES	12
BIBLIOGRAPHY	25
APPENDIX A: SUMMARY OF ADSORPTION ISOTHERMS	47
APPENDIX B: GIS ANALYSIS OF THE DISTRIBUTION AND ESTIMATED CO₂ STORAGE VOLUME OF THE DEVONIAN SHALE IN KENTUCKY	62
APPENDIX C: CNR 24752 ELK HORN COAL	70

LIST OF TABLES

Table 1. Gas storage capacity, total carbon (TC), total organic carbon (TOC), and vitrinite reflectance data for completed samples.....	11
Table 2. Summary of CO ₂ adsorption capacity in standard cubic feet per ton at selected pressures.....	11

LIST OF 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	12
Figure 2. General structure of the Devonian shale, showing presence of shale in the subsurface (shading).	12
Figure 3. Distribution and nomenclature of Devonian shales of Kentucky (Hamilton-Smith, 1993, p. 3).	13
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.	14
Figure 5. Nomenclature of Mississippian and Devonian shales of eastern Kentucky and key to names and codes used for intervals sampled.	15
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.	16
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.	17
Figure 8. Mean random reflectance ($R_{0 \text{ random}}$).....	18
Figure 9. 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).	18
Figure 10. Summary of adsorption isotherms by formation.....	20
Figure 11. Average calculated adsorption capacities by formation at selected pressures.....	21
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.....	22
Figure 13. Typical whole rock X-ray diffraction trace of the Devonian shale (upper part, well id 107928, Figure 7).	23
Figure 14. Preliminary estimated CO ₂ storage capacity per square kilometer (in million tons) in the areas of deeper ($\geq 1,000$ feet) and thicker (≥ 50 feet) Devonian shale.....	24

Executive Summary

Increased emissions of CO₂, 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 CO₂. 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, CO₂ is preferentially adsorbed, displacing methane at a ratio of two for one. Black shales may similarly desorb methane in the presence of adsorbing CO₂. If this is the case, black shales may be an excellent sink for CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ adsorption capacity ranges from 37 to 2,078 standard cubic feet CO₂ 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 CO₂ 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 CO₂, and their extensive occurrence in Paleozoic basins across North America would make them an attractive regional target for economic CO₂ 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
- NE/SE Combined GSA Section Meeting, March 25-27, 2004, Washington, DC
- 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 CO₂ injection, and Burlington Resources is currently evaluating the utility of CO₂ injection to enhance recovery of methane from coal. Results from these tests have shown that CO₂ injection and co-production of coalbed methane is technically and economically feasible. Since 1996, over 57 million m³ of CO₂ has been sequestered in Cretaceous coal of the San Juan Basin, New Mexico. The question is: can Devonian gas shales adsorb sufficient amounts of CO₂, making them significant targets for CO₂ 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 CO₂ 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 CO₂ 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 CO₂ is beyond the scope of this project and will be the subject of any subsequent CO₂ 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 millidarcy 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 CO₂ 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 CO₂. 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 (SO₂); carbon compounds are oxidized to CO₂. From the combustion system, sample gases pass through two tubes containing magnesium perchlorate (MgClO₄), which removes moisture, and then are routed to the infrared (IR) detection cells. A sulfur IR cell measures the amount of SO₂ present in the gas stream, and a carbon IR cell does the same for CO₂. All molecules, with the exception of bipolar species (e.g., N₂, H₂, O₂), 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 CO₂ sorption capacity. Mean random reflectance ($R_{0\text{random}}$) 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 ($R_{0\text{max}}$) 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 ± 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 CO₂ 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 CO₂, 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 CO₂ adsorption capacity data. Preliminary estimates were compiled using a uniform, minimum CO₂ 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 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 Etensohn (1980). Initial calculations indicate that 91×10^{12} cubic feet (2.6×10^{12} cubic meters) of CO_2 could be sequestered in the Lower Huron using a Langmuir volume of 67.6 scf/ton ($2.1 \text{ m}_3/\text{tonne}$; 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.

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Tables

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

Sample	Formation	Reported		TC as rec'd	TOC (acid*)	R _{0random}
		CO ₂ scf/ton	CO ₂ psia			
107928-1	Upper Ohio	37.5	681.1	1.67	0.69	1.55
107928-2	Lower Huron	67.6	243.7	3.94	2.95	1.48
107928-3	Lower Ohio	34.6	253.1	3.55	1.60	1.59
121774-1	Ohio Shale	126.5	989.8	6.15	3.66	1.10
124789-1	Upper Ohio	740.8	6419.1	4.41	3.26	0.78
124789-2	Lower Huron	2077.6	14283.5	5.69	4.62	0.81
124789-3	Lower Ohio	116.2	957.9	3.27	1.78	0.83
123486-1	Upper Ohio	228.9	2230.4	3.64	2.44	0.78
123486-2	Lower Ohio	309.3	2106.0	5.00	4.13	0.82
121162-1	Ohio Shale	164.2	1561.3	2.51	2.37	0.85
121464-1	Upper Ohio	52.6	708.9	1.33	1.18	1.52
121464-2	Lower Huron	248.7	751.2	4.21	3.60	1.52
121464-3	Lower Ohio	108	819	2.81	2.31	1.51

* 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 CO₂ adsorption capacity in standard cubic feet per ton at selected pressures.

Sample	FM	PSIA		
		300	400	500
121162-1	Ohio Shale	26.5	33.5	39.8
121774-1	Ohio Shale	29.4	36.4	42.5
Average	Ohio Shale Undifferentiated	27.9	34.9	41.1
107928-1	Upper Ohio	11.5	13.9	15.9
121464-1	Upper Ohio	15.6	19	21.8
124789-1	Upper Ohio	33.1	43.5	53.5
Average	Upper Ohio Shale	20.1	25.4	30.4
107928-2	Lower Huron	37.3	42	45.4
121464-2	Lower Huron	71	86.4	99.4
124789-2	Lower Huron	42.7	56.6	70.3
Average	Lower Huron	50.3	61.7	71.7
107928-3	Lower Ohio	18.8	21.2	23
121464-3	Lower Ohio	29	35.4	40.9
124789-3	Lower Ohio	27.7	34.2	39.9
Average	Lower Ohio Shale	25.1	30.3	34.6
Average	Overall	31.1	38.4	44.8

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 CO₂.

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 CO₂ storage capacity per square kilometer (in million tons) in the areas of deeper ($\geq 1,000$ feet) and thicker (≥ 50 feet) Devonian shale.

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Appendix A: Summary of Adsorption Isotherms

107928-1 3600-4000 ft. Ohio Shale (upper part)

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
61	2.6
141	6.1
209	8.6
262	11.0
326	13.1
395	15.0
484	16.7
589	17.9
811	18.6

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	37.5
Pressure (PSIA)	681.1

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.88 Density g/cc 2.756

107928-2 4400-4600 ft. Lower Huron Member

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
47	8.9
109	19.7
172	27.6
252	35.9
315	41.2
383	45.1
469	46.8
572	48.0
803	48.7

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	67.6
Pressure (PSIA)	243.7

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.97 Density g/cc 2.660

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

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
49	5.3
109	9.9
177	13.5
248	17.4
320	19.5
391	22.4
483	24.1
590	24.8
806	25.0

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	34.6
Pressure (PSIA)	253.1

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.98 Density g/cc 2.749

**121774-1A 3500-3720 ft. Ohio Shale
(Undifferentiated)**

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
23	2.9
50	6.4
82	9.8
103	11.8
130	14.2
185	18.9
251	24.8
321	31.3
392	37.2
512	48.4
705	68.9

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	126.5
Pressure (PSIA)	989.8

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

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

RN124789 1A 2680-2990 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
26	3.1
55	6.2
76	8.3
111	12.1
133	15.4
191	22.3
259	29.6
334	37.7
402	43.2
517	54.9
595	61.6

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	740.8
Pressure (PSIA)	6419.1

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.49 Density g/cc 2.597

RN124789 S2A 2990-3110 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
29	3.9
45	6.7
68	10.4
94	14.0
122	17.4
176	24.4
240	34.0
309	44.4
380	54.0
496	69.8
602	96.9

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	2077.6
Pressure (PSIA)	14283.5

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

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

RN124789 3A 3110-TD

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
32	4.2
49	6.0
74	8.2
110	11.4
136	13.6
193	17.9
253	23.6
326	30.4
394	35.6
512	45.7
663	60.3

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	116.2
Pressure (PSIA)	957.9

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.77 Density g/cc 2.679

RN123486 #1 341OHIOU 2600-3700 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
22	2.4
45	4.5
73	7.0
99	9.2
126	12.0
183	17.4
249	23.8
321	29.2
394	34.0
515	42.9
593	54.7

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	228.9
Pressure (PSIA)	2230.4

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.66 Density g/cc 2.631

RN123486 S2 341OHIOL 3070-3210 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
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

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	309.3
Pressure (PSIA)	2106.0

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.96 Density g/cc 2.573

121162 OHIO UPPER 3410-3810 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
14	1.6
40	4.3
65	6.6
111	10.5
127	11.9
192	17.0
247	22.2
312	28.6
381	32.6
498	44.5

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	164.2
Pressure (PSIA)	1561.3

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.79 Density g/cc 2.669

121464 OHIO Upper 3200-3300 ft,

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
19	1.6
49	3.6
78	5.0
100	6.1
159	8.9
193	10.5
250	13.7
316	17.2
384	18.9
501	24.2

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	52.6
Pressure (PSIA)	708.9

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

Isotherm Temperature: 86.0 °F
 Goodness of fit of Langmuir regression: 0.82 Density g/cc 2.694

121464 HURNL 4300-4380 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
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

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	248.7
Pressure (PSIA)	751.2

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

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

121464 OHIO Lower 4580-4980 ft.

Pressure (PSIA)	Adsorbed gas (ft ³ /ton)
	<i>In-Situ Conditions (Equilibrium Moisture)</i>
27	3.2
42	5.6
84	10.4
99	11.9
123	14.0
176	18.5
240	24.6
310	29.5
380	34.5
493	48.3

Langmuir Parameters

	<i>In-Situ Conditions (Equilibrium Moisture)</i>
Vol. (ft ³ /ton)	108.0
Pressure (PSIA)	819.0

SUMMARY OF ADSORPTION ANALYSES IMP. UNITS

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

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.

```
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_location.location_index =
dbo_geographic_region.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));
```

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

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:

$$Tons_{shale} = volume * density$$

and

$$MMTons_{shale} = \frac{thickness * area * density}{1000000}$$

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

$$MMTons_{shale} = \frac{thickness * \frac{0.3048m}{ft} * (1000m)^2 * density * 1.102}{1000000} \quad \text{Eq. 1.}$$

where:

<i>thickness</i>	= thickness of shale in feet
1000	= cell size in meters
<i>density</i>	= 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, $CfMMTons$, would be one of:

2.5 g/cc (log estimated density for Lower Huron)	= 0.840
2.6 g/cc (log estimated density for upper part of shale)	= 0.873
2.65 g/cc (log handbook typical shale density)	= 0.890

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

$$[Target] * CfMMTons.AsGrid = [MMTons]$$

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 CO₂ sequestered requires an additional factor based on the gas content per ton of shale from CO₂ adsorption data. Using a gas content of 1 standard cubic foot of CO₂ per ton and 17.25¹ thousand cubic feet (Mcf) CO₂ per ton of CO₂, there will be 57.97 tons of CO₂ per million tons of shale.

$$TonsCO_2 = \frac{ft^3_{CO_2}}{ton_{shale}} * 1000000 * \frac{Mcf}{1000ft^3_{CO_2}} * \frac{ton_{CO_2}}{17.25Mcf} = 57.97 \quad \text{Eq. 2}$$

The sequestration volume in tons of CO₂ can now be considered a function of thickness, shale density, and adsorbed gas content, or:

$$TonsCO_2 = 57.97 * CfMMTons * thickness * gascontent$$

Multiplying the 57.97 and $CfMMTons$ provides a single factor that varies only with density:

Factor = 48.69 at density equals 2.5 g/cc
Factor = 50.61 at density equals 2.6 g/cc
Factor = 51.59 at density equals 2.65 g/cc

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 CO₂ 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 CO₂ per cell is 2024.3 per foot of shale thickness, thus:

$$[Target] * (2024.3).AsGrid = [CO2Tons]$$

¹ 17.25 Mcf CO₂ per ton CO₂ 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.

Summary by county of potential sequestration totals (gas content 40 scf/ton, shale density 2.6 g/cc, cell size 1,000 meters):

Name	Basin	Count	Min	Max	Mean	MMTonsCO2
BELL	160	949	0.24	1.52	0.51	486.8
BOYD	160	420	1.03	1.70	1.39	583.9
BREATHITT	160	1293	0.38	1.05	0.60	775.2
CARTER	160	329	0.34	1.26	1.05	346.6
CLAY	160	1236	0.24	0.48	0.35	433.2
ELLIOTT	160	292	0.29	1.14	0.92	267.2
FLOYD	160	1040	0.27	1.79	1.42	1,474.4
GREENUP	160	339	0.99	1.38	1.24	421.7
HARLAN	160	1211	0.31	1.17	0.76	918.6
JACKSON	160	275	0.21	0.34	0.25	69.4
JOHNSON	160	657	0.86	1.67	1.28	839.8
KNOTT	160	918	0.78	1.42	1.06	969.9
KNOX	160	1017	0.20	0.47	0.31	318.5

Name	Basin	Count	Min	Max	Mean	MMTonsCO2
LAUREL	160	1146	0.16	0.38	0.22	255.7
LAWRENCE	160	1089	0.20	1.85	1.37	1,490.6
LEE	160	232	0.22	0.50	0.35	81.6
LESLIE	160	1066	0.38	0.79	0.55	590.8
LETCHER	160	894	0.21	1.70	1.13	1,012.2
MAGOFFIN	160	793	0.63	1.20	0.92	730.8
MARTIN	160	631	1.23	2.32	1.76	1,113.1
MCCREARY	160	703	0.10	0.24	0.15	107.8
MENIFEE	160	16	0.37	0.42	0.39	6.2
MORGAN	160	710	0.25	1.19	0.70	496.8
OWSLEY	160	497	0.13	0.44	0.34	168.0
PERRY	160	892	0.37	1.04	0.71	630.4
PIKE	160	2056	0.82	3.60	2.17	4,467.3
POWELL	160	7	0.31	0.34	0.32	2.2
ROCKCASTLE	160	4	0.19	0.21	0.20	0.8
ROWAN	160	2	0.54	0.54	0.54	1.1
WHITLEY	160	1161	0.16	0.70	0.22	261.1
WOLFE	160	525	0.20	0.81	0.45	237.1
Appalachian	160 Total					19,558.9
MARSHALL	250	29	0.39	0.56	0.48	13.9
Jackson Purchase	250 Total					13.9
EDMONSON	300	670	0.12	0.40	0.24	157.5
HARDIN	300	220	0.13	0.18	0.16	35.3
HART	300	178	0.11	0.20	0.15	26.4
MEADE	300	106	0.18	0.22	0.20	21.6
PULASKI	300	58	0.14	0.18	0.16	9.3
WARREN	300	424	0.12	0.38	0.20	84.0
Cincinnati Arch	300 Total					334.2
BRECKINRIDGE	315	1426	0.10	0.26	0.19	274.8
BUTLER	315	1130	0.11	0.41	0.28	320.3
CALDWELL	315	898	0.27	0.67	0.48	430.0
CHRISTIAN	315	1870	0.11	0.58	0.25	470.0
CRITTENDEN	315	968	0.31	0.90	0.66	634.1
DAVISS	315	1255	0.12	0.46	0.32	404.1
GRAYSON	315	1277	0.12	0.49	0.27	343.6
HANCOCK	315	516	0.15	0.54	0.29	150.5
HENDERSON	315	1233	0.11	0.64	0.45	560.8
HOPKINS	315	1464	0.14	0.64	0.41	595.7
LIVINGSTON	315	696	0.42	0.67	0.60	415.6
LOGAN	315	966	0.12	0.25	0.19	183.1
LYON	315	620	0.28	0.59	0.46	284.8
MCLEAN	315	671	0.14	0.56	0.39	259.9
MUHLENBERG	315	1266	0.12	0.59	0.34	425.4
OHIO	315	1549	0.16	1.09	0.37	573.4
TODD	315	879	0.10	0.31	0.18	156.9
TRIGG	315	848	0.16	0.34	0.24	200.6
UNION	315	953	0.57	0.81	0.69	657.7
WEBSTER	315	878	0.17	0.68	0.51	445.1
Illinois Basin	315 Total					7,786.5
	Grand Total					27,693.5
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 CO₂ 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'

Era	Formation	Code	Top (feet)	Condition	Fluoresce	Comments	Shipped
Mssp	Little Lime	332LTLM	1698				
	Pencil Cave	332PCCV	1735				
	Big Lime	332BIGL	1739				
	Borden	337BRDN	1954				
	Sunbury	339SNBR	2249				
	Berea	339BREA	2283				
Devonian	Ohio Shale	341OHIO	2346				
	Cleveland Sh Mbr	341CLVD	2346				
	Core 10	341CLVD	2370	Intact	No	dry, faint odor	Yes
	Three Lick Bed	341TLBD	2452				
	Core 9	341TLBD	2455	Intact	No	light gray	Yes
	Core 8	341TLBD	2465	Intact	No	odor, dark oily black, slick, sticky feel, but not wet	Yes
	Upper Huron Mbr	341HURNU	2488				
	Core 7	341HURNU	2530	Intact	No	slight odor, dark oily black as in core 8	Yes
	Middle Huron Mbr	341HURNM	2543				
	Core 6	341HURNM	2630	Broken	No	slight odor, waxy feel, but not wet	No
	Lower Huron Mbr	341HURNL	2726				
	Core 5	341HURNL	2730	Intact	No	dry, somewhat mottled	Yes
	Core 4	341HURNL	2760	Intact	No	dry, somewhat mottled	Yes
	Core 3	341HURNL	2780	Intact	No	dry, approx. 0.5cm pyrite clast, possible faint odor	Yes
	Core 2	341HURNL	2835	Broken	No	oily, strong odor	No
	Olentangy	341OLNG	2838				
	Core 1	341OLNG	2900	Broken	No	oily, strong odor	No

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).