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 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 electron capture spectroscopy log has been acquired to investigate possible correlations between adsorption capacity and mineralogy.

Average random vitrinite reflectance ($R_{0random}$) 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, the extensive occurrence of shales 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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Introduction

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 CO_2, the most important greenhouse gas [1]. Naturally occurring organic matter (kerogen) is a microporous material that possesses a very high surface area and hence sorption capacity for gas. The question is: can Devonian gas shales adsorb sufficient amounts of CO_2, that they might be significant targets for CO_2 sequestration?

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 seqestration project well in Mason County, W. Va.

The Ohio Shale is subdivided into seven recognizable units: 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. A summary of reservoir data for the Big Sandy Gas Field is available in the "Atlas of Major Appalachian Gas Plays" [2]. 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.

Methods

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.

To investigate any relation between organic content and CO_2 sorption capacity, total organic carbon content (TOC) was determined. For total organic carbon analyses, duplicate sample splits were crushed to a maximum particle size of 200 microns (–60 mesh): 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.

To measure thermal maturity, mean random reflectance on dispersed vitrinite particles in the samples was determined on a Zeiss USMP incident light microscope calibrated using glass standards of known reflectance. Maximum vitrinite reflectance values can be estimated by multiplying the mean random measurements by 1.066 [3].

Adsorption analyses were performed using a high-pressure volumetric adsorption technique similar to that described by Mavor and others [4]. Isotherms were measured on a custom-made apparatus. A known volume of gas within a reference cell is used to dose a sample cell. 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 (Peng Robinson equation of state). Following dosing of the sample cell, the pressure drops until equilibrium is reached. 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 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).

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. The sidewall core plugs are being saturated with methane and will subjected to simulated injection of CO_2. Laboratory setup and analyses are similar to the standard procedure for obtaining adsorption isotherms.

Results to Date

Twenty-six samples have been collected from seven wells, including three cuttings samples and 10 sidewall cores from the Columbia Natural Resources No. 24752 Elkhorn Coal Corporation well in Knott County. In addition to the sidewall cores, electron capture spectroscopy and lithodensity logs has been acquired for the well. Data for completed analyses are presented in Table 1.

Adsorption isotherms for these samples are presented in Figure 2. 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, and Figure 3 presents calculated adsorption capacities at three pressure values expected to be typical of the range of observed Devonian shale gas reservoir conditions.

Preliminary Interpretation and Conclusions

Initial estimates of CO_2 sequestration capacity have been calculated using selected data. The sequestration volume of the Lower Huron was estimated using areal distribution and thickness data from Dillman and Ettensohn [9] and indicate 91 x 10^{12} cubic feet (2.6 x 10^{12} cubic meters) of CO_2 could be sequestered in the Lower Huron. Assuming 30 percent of this theoretical saturation, approximately 1.6 billion tons (1.5 billion metric tonnes) of CO_2 could be sequestered. Using a GIS technique, estimated initial CO_2 sequestration capacity of the Devonian shale in Kentucky is 27.7 billion tons (25.1 billion metric tonnes) (Figure 4) in shale at least 1,000 feet deep and 50 feet thick.

Preliminary data indicate that black, organic-rich gas shales can serve as targets for sequestration of significant volumes of anthropogenic CO_2. 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 CO_2 would contribute to a long-term increase in the supply of that resource.

Acknowledgments

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References

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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*)**	**$R_{0random}$**
		Langmuir volume (CO_2 scf/ton)	**Langmuir pressure (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 CO_2 adsorption capacity in standard cubic feet per ton at selected pressures.

Sample	Formation	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

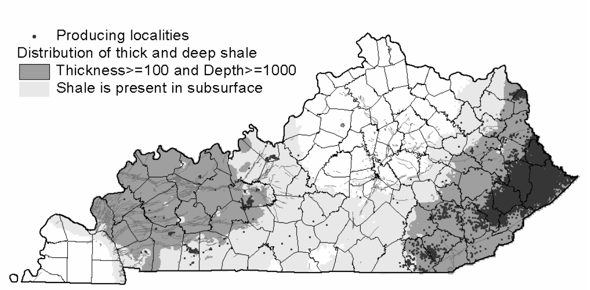

Figure 1. Distribution of the Devonian shale in Kentucky, showing the occurrence of deeper and thicker shale with possibly greater potential for geologic sequestration of CO_2.

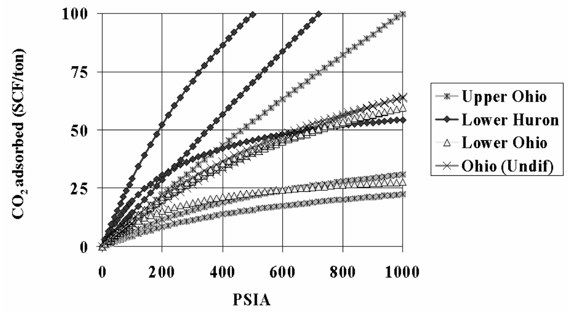

Figure 2. Summary of adsorption isotherms by formation.

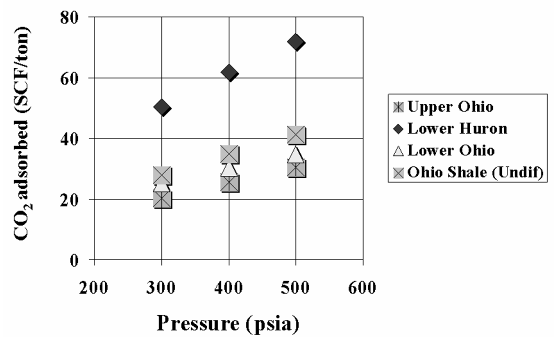

Figure 3. Average calculated adsorption capacities by formation at selected pressures.

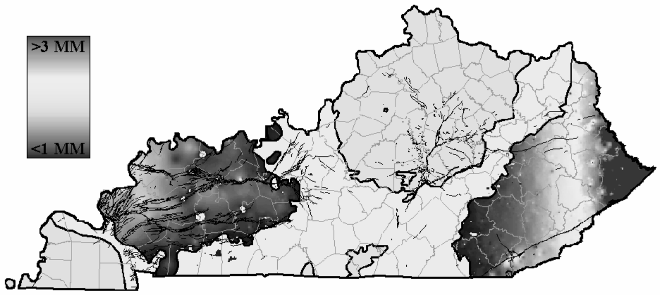

Figure 4. Preliminary estimated CO_2 storage capacity per square kilometer (in million tons) in the areas of deeper (>=1,000 feet) and thicker (>=50 feet) Devonian shale