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

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Abstract

Proposed carbon management technologies include geologic sequestration of CO₂. A possible, but untested, strategy is to inject CO₂ into organic-rich shales of Devonian age. Devonian black shales underlie approximately two-thirds of Kentucky and are generally thicker and deeper in the Illinois and Appalachian Basin portions of Kentucky. The Devonian black shales serve as both the source and trap for large quantities of natural gas; total gas in place for the shales in Kentucky is estimated to be between 63 and 112 trillion cubic feet. Most of this natural gas is adsorbed on clay and kerogen surfaces, analogous to the way methane is stored in coal beds. In coals, it has been demonstrated that CO₂ is preferentially adsorbed, displacing methane at a ratio of two to one. Black shales may similarly desorb methane in the presence of CO₂. If black shales similarly desorb methane in the presence of CO₂, the shales may be an excellent sink for CO₂ with the added benefit of serving to enhance natural gas production.

The concept that black, organic-rich Devonian shales could serve as a significant geologic sink for CO₂ is the subject this research. To accomplish this investigation, drill cuttings and cores will be selected from the Kentucky Geological Survey Well Sample and Core Library. CO₂ adsorption analyses will be performed in order to determine the gas-storage potential of the shale and to identify shale facies with the most sequestration potential. In addition, new drill cuttings and sidewall core samples will be acquired to investigate specific black-shale facies, their uptake of CO₂, and the resultant displacement of methane. Advanced logging techniques (elemental capture spectroscopy) will be used to investigate possible correlations between adsorption capacity and geophysical log measurements.

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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 (TOC), vitrinite reflectance ($R_{0\text{ random}}$), 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.

Introduction

Since the discovery of natural gas production from the Devonian shales of Kentucky between 1858 and 1865, these carbonaceous shales have constituted an important energy resource in Kentucky. Thick and deep sequences of shale exist in both the Illinois and Appalachian Basins (Figure 1). Greenhouse gases, CO₂ emissions in particular, are being linked to global climate change. If regulations are adopted that require limiting CO₂ emissions, disposal strategies must be identified. Using CO₂ flooding of coals as a model, the large component of adsorbed natural gas in organic-rich shales suggest that black shale might be an attractive sequestration target.

The project is concentrating on the Devonian Ohio shale of eastern Kentucky (Figure 2). This area is both the most active area (number of wells drilled over the past 5 years) and the most prolific natural gas producing area in the state accounting for 98 percent of Kentucky's gas production. The Kentucky Geological Survey maintains an extensive collection of cuttings recovered during oil and gas well drilling in the Well Sample and Core Library.

Figure 1. Map of the 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. Map showing distribution and nomenclature of Devonian shales of Kentucky (Hamilton-Smith, 1993, p. 3)

Experimental

- 1) The sampling protocol has been modified to eliminate washing and air-drying of drill cuttings.

Washing the samples resulted in the loss of too much material. In one case, a substitute for a selected well had to be chosen because insufficient material was available for sampling after washing. Eliminating air drying of the samples saves about one week per each well sampled.

- 2) Unwashed sets of recently acquired drill cuttings have been identified. These samples are being sorted and processed to place them in permanent storage bags and boxes.
- 3) The well sample data spreadsheet has been matched to the main oil and gas well record database in order to compile a GIS coverage of these data (**Figure 4**). The GIS was used to select wells that best represent a uniform coverage of the study area and provide information useful for targeting the area to be sampled by sidewall coring in year 2.

Results and Discussion

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 3). 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. Where present, these shales will be composited as a separate sample.

A database of candidate Devonian shale wells for sampling was compiled. Kentucky statutes [KRS 353.660(2)] provide the Survey with the right to request well samples. In anticipation of this project, samples were requested for proposed Devonian shale penetrations in eastern Kentucky. Paper records of well samples received were requested from staff of the well cuttings and cores repository and entered into an Excel spreadsheet. A total of 595 candidate wells have been identified (**Figure 4**). Geophysical logs from these wells are being scanned to assist in stratigraphic interpretation. A GIS will be used to select wells that best represent a uniform coverage of the study area and provide information useful for targeting the area to be sampled by sidewall coring in year 2.

While processing unwashed and cataloged drill cuttings at the Well Sample and Core Library, several pallets of recently received, unwashed, but uncataloged, cuttings were located. These drill cuttings have been identified and incorporated into the GIS for sampling.

The final distribution of wells selected for sampling is illustrated in Figure 5. A list of these wells is provided in Table 1.

Table 1. Wells to sample for the Devonian Shale CO₂ Sequestration project.

PERMIT	OPERATOR	WELL	FARM_NAME	COUNTY	SEC	LTR	NUM	TOTAL_	TDFM
84653	ASHLAND EXPLORATION, INC	60	FORD MOTOR COMPANY	Pike	19	M	88	6130	361SQTC
90973	BRADLEY, CHARLES R DBA BASIN ENE	1	NORDMAN, EARLENE	Magoffin	1	O	79	2390	357CBOC
91129	KINZER, J W	1003	PIKE LETCHER LAND CO	Letcher	4	I	81	3814	341OHIO
91151	EQUITABLE PRODUCTION COMPANY	KF-4448	EQUITABLE PRODUCTION CO	Floyd	25	K	83	3964	341OLNG
91182	EQUITABLE PRODUCTION COMPANY	KL4390	HOPKINS, JC & VALENTINE	Floyd	4	N	82	2358	341OLNG
91355	KINZER, J W	1052	KINZER, J W	Pike	20	M	90	5199	347HDBG
91796	PENN-VIRGINIA OIL & GAS CORP	11	KENTENIA	Harlan	7	D	73	4327	361ODVCU
92640	EQUITABLE PRODUCTION COMPANY	KL4-504695	LOWE, A HEIRS	Pike	20	N	84	3639	341OLNG
92647	ENERGY ASSOCIATES, INC	1	ASHER, IDA ET AL	Clay	8	G	72	2755	357CLNT
92715	COLUMBIA NATURAL RES, INC	24526	BUSH, JOHN ET AL	Floyd	9	L	83	3268	341OHIO
93241	EQUITABLE PRODUCTION COMPANY	505045	EVANS, E J	Knott	12	L	79	2770	341HURNL
93411	EQUITABLE PRODUCTION COMPANY	505040	EQUITABLE PRODUCTION COMPANY	Breathitt	7	M	78	2760	341OLNG
93453	EQUITABLE PRODUCTION COMPANY	504725	EQUITABLE PRODUCTION CO	Knott	11	I	78	3550	341OLNG
93520	EQUITABLE PRODUCTION COMPANY	504984	EQUITABLE PRODUCTION CO	Knott	9	J	77	3682	341OLNG
93560	EQUITABLE PRODUCTION COMPANY	504384	THE ELK HORN COAL CORP	Floyd	22	M	81	2510	341OLNG
93762	C D & G ENT - JOHNSON, GARY C	1	MCGINNIS, BASIL ET AL	Martin	19	P	83	2879	341OHIO
93844	BRADLEY, CHARLES R DBA BASIN ENE	1	RIDDLE, TROY	Perry	6	G	78	3905	341OHIO
94045	COLUMBIA NATURAL RES, INC	24875	KENTUCKY BERWIND LAND CO	Pike	14	K	87	4975	341OHIO
94086	INTERSTATE NATURAL GAS CO	4	DAVIS, IDA	Knott	24	K	81	3190	341OHIO
94088	EQUITABLE PRODUCTION COMPANY	505313	EQUITABLE PRODUCTION CO	Pike	16	K	86	4182	341OLNG
94107	EQUITABLE PRODUCTION COMPANY	505333	EQUITABLE PRODUCTION CO	Pike	14	L	86	4360	341OLNG
94174	COLUMBIA NATURAL RES, INC	23798	HAYS, LUTITIA ET AL	Knott	8	J	79	3256	341OHIO
94175	EQUITABLE PRODUCTION COMPANY	504790	TIERNEY, LAWRENCE E	Pike	19	N	86	4150	341OLNG
94210	EQUITABLE PRODUCTION COMPANY	565386	EQUITABLE PRODUCTION CO	Pike	13	J	84	4620	341OLNG
94229	COLUMBIA NATURAL RES, INC	24945	THE ELK HORN COAL CORP / HUNT	Floyd	4	L	83	3126	341OHIO

Figure 3. Chart showing nomenclature of Mississippian and Devonian shales of eastern Kentucky.

Figure 4. Initial distribution of Devonian shale drill cuttings sample sets.

Figure 5. Eastern Kentucky Devonian Shale CO2 Sequestration sample locations.

The Kentucky Well Sample and Core Library is a facility housing a legacy data set of subsurface information for the Commonwealth. Drill cuttings are received at the warehouse, cataloged, and shelved while awaiting processing. Sample bags are identified by well and depth information and roughly sorted. The contents of each bag are emptied into a 160 mesh copper sieve with a serial identifier. For each sample bag, a sample label is prepared with the sieve number, footage, and catalogue number. This label is mounted on a plastic insert that will become a permanent part of the sample collection. Once loaded into the sieves, the samples are placed on a tray and run through a conveyor driven sample washer. For this project, the drying oven is turned off and all samples are air-dried. After drying, the plastic identifying tags are matched to the sieves. The tag and cuttings are stored together in a self-sealing polyethylene bag. The identified bags are then sorted by depth and loaded into corrugated boxes for storage in the library.

For this project, the intervals to be samples are identified from the drillers' logs and geophysical logs on file (see **Figure 4** for a type log). Equal amounts of cuttings from each interval are incorporated into the composite sample for adsorption and petrographic analysis. If there are multiple sample bags for the same interval, only one bag is sampled. The composite samples are mixed and split into fractions as required for each procedure.

Unwashed drill cuttings that have been checked in and cataloged

Pallet of unwashed drill cuttings as received (not cataloged)

Drill cuttings readied for sorting and processing.

Sorting samples in preparation for loading into polyethelyene sample bags.

Sorted drill cuttings are packed into individual bags

Leah Barth collecting composite sample for CO₂ adsorption and petrographic analyses

Splitting composite sample for petrographic and adsorption analyses

Cortland Eble examining samples for petrographic analysis

Conclusion

Collecting drill cuttings for composite sampling is proceeding. Uncatalogued sample sets are being identified for incorporation into the project. The sampling procedures have been revised to eliminate washing in order to increase the amount of available material in the drill cuttings. Geophysical logs are being correlated to direct sampling efforts. Sample sets are being delivered to partners for analysis.

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