**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.

Table of Contents

Disclaimer	i
Abstract.....	ii
Table of Contents	iii
Figures	iii
Executive Summary.....	1
Introduction	2
Experimental.....	3
Results and Discussion	4
Conclusion.....	6
Bibliography	7

Figures

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 CO ₂	2
Figure 2. Map showing distribution and nomenclature of Devonian shales of Kentucky (Hamilton-Smith, 1993, p. 3)	3
Figure 3. Chart showing nomenclature of Mississippian and Devonian shales of eastern Kentucky.	5

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. The Devonian Shale Sequestration project began the compilation of a bibliography to identify previous work and provide supporting data for continued research.

To investigate the concept that black, organic-rich Devonian shales, like coals, could serve as significant geologic sinks for CO₂. A sampling protocol has been established that uses drill cuttings available at the Kentucky Geological Survey. Identifying candidate samples and selecting and preparing those samples for analysis is in process. 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.

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, and CO₂ emissions in particular, are being linked to global climate change. Should regulations require limiting CO₂ emission be adopted, disposal sites must be identified. With a large component of adsorbed natural gas it is suggested that organic-rich shales 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) Sampling protocol was established for drill cuttings. Drill cuttings for 30 wells were proposed to be sampled. Communications with R. Marc Bustin and Cortland Eble indicated a total of approximately 150 grams of shale were required for CO₂ adsorption and petrographic analysis. Samples will be selected from recently received, unwashed, and unprocessed drill cuttings through the Devonian black shale of eastern Kentucky. These criteria were selected to:
 - a) Minimize the effects of sample oxidation
 - b) Minimize sample alteration or loss of volatiles resulting from oven drying
 - c) Maximize the amount of sample material available to both meet the required sample cut and leave sufficient material for the remaining sample to be incorporated into the permanent collection
- 2) Compile a database of candidate Devonian shale wells for sampling. 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. Wells from this set with geophysical logs on file are being identified.

- 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. This 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.

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 dark gray to black samples characteristic of the Lower Huron Member. In some areas of the Big Sandy Gas Field, the Olentangy and Rhinestreet shales are present but have a somewhat lesser organic content.

Leah Barth is a student pursuing a degree in geology at the University of Kentucky. She was hired and will provide data entry support and will be collecting and preparing the Devonian shale samples for analysis.

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The industry partner, Columbia (now NiSource), has been contacted to keep them abreast of project status and to monitor their drilling plans for candidate wells to be sampled with sidewall coring in year 2.

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

Conclusion

The Devonian Shale Sequestration project is underway. A bibliography is being compiled. Sampling procedures have been established and drill cuttings are being identified and processed.

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