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

As sets of drill cuttings are being identified and processed, it has been noted that significant volumes of material are being lost during the washing process. We are considering modifying the sampling protocol to collect cuttings before washing; a panel will be convened to discuss this change. Identifying candidate samples and selecting and preparing those samples for analysis is continuing. 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, 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 is being evaluated to determine if washing and air drying the available drill cuttings is required. Eliminating these steps will speed sample collection. A meeting of project advisors is being convened to discuss this modification.
- 2) A number of unwashed sets of recently acquired drill cuttings have been identified. These sample sets have not been checked in and are being inventoried for inclusion in the sample selection process.
- 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). 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. As they are identified, the new sample sets will be incorporated into the GIS.

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. As these sets of drill cuttings are being identified, they will be incorporated into the GIS and will be considered for sampling.

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

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

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 bag in the interval are incorporated into the composite sample for adsorption and petrographic analysis. The composite samples are mixed and split into fractions as required for each procedure.

Unwashed samples that have been checked in and cataloged

Pallet of unwashed samples (not cataloged)

Sorting samples in preparation for washing

Sample washing machine

Ready for washing

Sieves used for washing, note serial numbers

Loading samples into sieves and marking them

Under the water jets in the washer

Washed samples ready for air drying

Dried and sorted samples are packed into individual bags

Leah Barth collecting composite sample for CO₂ adsorption analysis

Splitting composite sample for petrographic and adsorption analyses

Conclusion

Collecting drill cuttings for composite sampling is proceeding. Uncatalogued sample sets are being identified for incorporation into the project. The sampling procedures are being reconsidered to eliminate washing in order to increase the amount of available material in the drill cuttings.

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