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Full Length Article

Quantifying dry supercritical CO_2-induced changes of the Utica Shale

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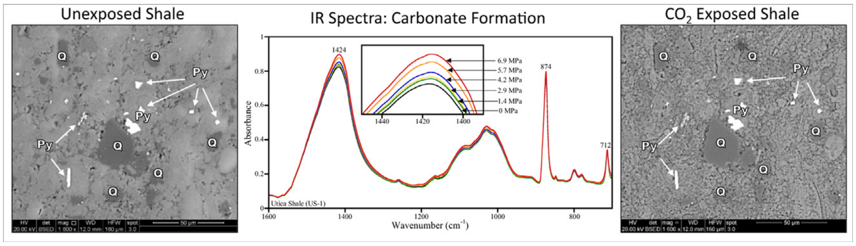
GRAPHICAL ABSTRACT



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ABSTRACT

Traditionally, shale formations have been studied as sealing layers that prevent vertical migration of hydrocarbons and CO_2 due to their low permeability and fracture porosity. Recent research has focused on storing CO_2 in hydrocarbon-bearing shale formations that have already undergone depletion through primary production and using CO_2 as a potential fracturing agent for unconventional reservoirs. The injected CO_2 will interact with shale components (i.e. clays, organic matter) and affect rock properties through chemical alteration, matrix swelling/shrinkage, and related geomechanical effects. As changes in rock properties will impact both anthropogenic CO_2 storage and hydraulic fracturing, it is imperative to increase our understanding of the CO_2-shale interactions. *In-situ* Fourier Transform infrared (FT-IR) spectroscopy coupled with high temperature and pressure capability was used to examine the interaction of dry CO_2 on Utica Shale, clay, and kerogen samples at the molecular scale and characterize vibrational changes of sorption bands sensitive to the gas-solid environment. The Utica Shale was also analyzed for micro and macro-scale chemical and physical changes before and after exposure to dry CO_2 at subsurface storage conditions using surface relocation techniques via high-resolution field-emission scanning electron microscopy (FE-SEM). Brunauer-Emmett-Teller (BET) surface area/pore size analysis and quantitative adsorption isotherms were applied to understand changes in surface area, pore volumes, and understand the storage potential of CO_2 in the Utica Shale sample. FT-IR and feature relocation via FE-SEM indicate carbonate formation and dissolution occurs in shale exposed to dry CO_2. Results indicate that etching and pitting occur, with minor calcite precipitation along the surface of the shale sample. Quantitative isotherm results indicate that shales with a higher content of kerogen and illite-smectite clays would be expected to have the highest CO_2 storage capacity provided these constituents were accessible for interaction.

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1. Introduction

As climate change becomes an increasingly critical environmental issue, efforts are being made to reduce or divert anthropogenic CO_2 emissions from the atmosphere with Geologic Carbon Sequestration (GCS). GCS is a process where anthropogenic CO_2 that has been captured, typically at the source where it is generated (e.g. fossil-fuel burning power plant), is injected and stored in the subsurface within various geologic formations such as saline formations, depleted oil and gas reservoirs, unmineable coal seams, basalts, and shale formations [35,36,55]. Additionally, CO_2 is being used as an agent to enhance oil recovery from conventional reservoirs and as a potential fracturing agent for unconventional reservoirs, where a portion of the CO_2 is stored in the subsurface as a result of these activities [14,58].

Due to the growth in shale hydrocarbon exploration, GCS in depleted shale formations is gaining interest [35,36,41,26]. Only hydrocarbon-bearing shale formations that have already undergone depletion through primary production, or are planned to be produced in the future, are considered as potential geologic sinks for CO_2. Levine et al. [26] listed the following criteria required for CO_2 storage in shales: (1) hydrocarbon production using horizontal drilling and stimulation via staged, high-volume hydraulic fracturing must occur prior to GCS operations, (2) CO_2 must be injected at depths sufficient to maintain CO_2 in a supercritical state (generally greater than 800 m), and (3) a seal must be present overlying the shale formation targeted for GCS. Storage of CO_2 in shale is expected to occur as a free phase within hydraulic and natural fractures and matrix pores and as a sorbed phase on organic and inorganic matter such as kerogen and clays. CO_2 has the potential to be utilized as a hydraulic fracturing fluid to reduce water use, increase hydrocarbon production, and create greater access to pore space [14,58]. Thus, understanding CO_2 interactions with shale provides insight into issues facing CO_2 storage and hydraulic fracturing activities. It is important to note that most unstimulated shales serve as reservoir seals for hydrocarbon reservoirs and for GCS. This means these reactions between CO_2 and shale will commonly occur at the interface between a storage formation and the overlying seal. The nature of these reactions will have implications related to possible leakage and long term storage potential.

The majority of research has focused on CH_4 sorption on the organic component in shales [42,43,44,30,60] with some work on CH_4 and CO_2 interactions on various clay components such as montmorillonite, kaolinite, and illite [27,45,20,46,56]. Ross and Bustin [44] examined controls for CH_4 in a suite of Jurassic and Devonian-Mississippian shales from western Canada in terms of organic content, inorganic components, and thermal maturity. They found that both organic and clay minerals such as illite were important for controlling CH_4 storage capacity. In general, reports on high-pressure CO_2 sorption isotherms on shales are sparse [41]. Busch et al. [3] examined the CO_2 sorption potential of a Muderong shale sample from Australia and its clay components – Ca-rich montmorillonite, Na-rich montmorillonite, illite, and kaolinite – at subsurface conditions relevant to storage. They found evidence for significant storage potential in shales that included physical sorption of CO_2 on clay minerals as well as CO_2 dissolution and geochemical reactions. Lahann et al. [23] examined the influence of CO_2 on the New Albany shale with high and low organic contents and high carbonate content and observed dissolution of carbonate-mineralized biogenic structures. Bacon et al. [1] provided the first field-scale modeling effort of CH_4 production and CO_2 injection to include both organic and clay sorption behavior in shale gas production models to improve accuracy. They found that the CO_2 sorption potential was similar for both organic matter and montmorillonite clay.

The objective of this work is to investigate the interaction of CO_2 with shale and identify and quantify chemical and physical alterations at the molecular and micro-scale. The shale being investigated is the Utica Shale first described by Emmons [7]. It was chosen for this study because the formation is being targeted for hydrocarbon production and it represents a potential reservoir for CO_2 storage. Specifically, this study focuses on characterizing the surface interactions of the interface between CO_2 and the Utica Shale with *in-situ* Fourier Transform infrared spectroscopy (FT-IR), feature relocation scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) surface area and pore size analysis, and quantitative adsorption isotherms at pressure and temperature conditions relevant for geological storage. We also examine surface interactions of primary individual constituents of the Utica Shale such as clays [illite-smectite, illite, chlorite, and kaolinite] and kerogen to further investigate the mechanism responsible for reactions at the CO_2-shale interface.

2. Materials and experimental methods

2.1. Utica Shale: Flat Creek Member (US-1)

The Utica Shale is a calcareous, organic-rich shale deposited in the Appalachian Basin during the Middle Ordovician Taconic Orogeny [51]. The typical depth for shale gas in the Utica ranges from 700 to 1800 m with an average net thickness of 150 m [51,15]. The Utica Shale (US-1) was collected in the state of New York from a stream bed outcrop of the Utica Shale Flat Creek Member (Table 1) and is considered over-mature [12,47]. Samples were collected from the interior of the outcrop to reduce weathering affects. The shale sample was stored in a nitrogen desiccator prior to characterization.

2.2. Clay samples

Clay samples – illite-smectite (ISCz-1), illite (IMt-2), chlorite (CCa-2), and kaolinite (KGa-1b) – were selected based on clays that were representative of the US-1 shale sample (Table 2). These clay standards were purchased from the Clay Mineral Society and used as received. Chlorite (10–20%), illite (55–70%), illite-smectite (15–25%), illite-chlorite (trace), and kaolinite (trace) are common clays found in the Middle and Upper Devonian shale units in the Appalachian basin [1,11]. Qualitative X-ray Diffraction (XRD) analysis of US-1 shown in Table 3 supports the findings in the literature. Smectite clays are not common in thermally mature shales as with increased burial depth and temperature; smectite is converted into illite via mixed layer illite/smectite formation. This process is known as smectite diagenesis or smectite illitization [38]. These samples represent a wide spectrum of clay mineral structures such as 1:1 repeating tetrahedral-octahedral (TO) layers (kaolinite), 2:1 alternating TOT layers (illite), mixed-layer (illite-smectite), and 2:1 + 1 alternating TOT layers (chlorite).

2.3. Kerogen

A kerogen sample (NAk-1) was analyzed to study the effects of organic matter which is prevalent in shale. Due to limited sample quantity of the Utica Shale, we were unable to extract enough kerogen for the sample characterization and measurements needed in this study. As a proxy for kerogen found in the Utica Shale, kerogen extracted from the New Albany Shale was provided by Maria Mastalerz at the Indiana Geological Survey. This kerogen (NAk-1) still contained some clay/quartz material as it is very difficult to extract pure kerogen from shale.

Table 1
Utica Shale sample information.

Basin	Description		Sample Location	
Appalachian	Utica Shale: Flat Creek Member	Stream Bed Outcrop	Latitude	Longitude
			42° 53′ 11″ N	74° 33′ 53″ W