U.S. DOE NETL Methodology for Estimating the Prospective CO₂ Storage Resource of Shales at the National and Regional Scale

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Abstract

While the majority of shale formations will serve as reservoir seals for stored anthropogenic carbon dioxide (CO₂), hydrocarbon-bearing shale formations may be potential geologic sinks after depletion through primary production. Here we present the United States-Department of Energy-National Energy Technology Laboratory (US-DOE-NETL) methodology for screening-level assessment of prospective CO₂ storage resources in shale using a volumetric equation. Volumetric resource estimates are produced from the bulk volume, porosity, and sorptivity of the shale and storage efficiency factors based on formation-scale properties and petrophysical limitations on fluid transport. Prospective shale formations require: 1) prior hydrocarbon production using horizontal drilling and stimulation via staged, high-volume hydraulic fracturing, 2) depths sufficient to maintain CO₂ in a supercritical state, generally >800 m, and 3) an overlying seal. The US-DOE-NETL methodology accounts for storage of CO₂ in shale as a fluid phase within fractures and matrix pores and as an adsorbed phase on organic matter and clays. Uncertainties include but are not limited to poorly-constrained geologic variability in formation thickness, porosity, existing fluid content, organic richness, and mineralogy. Knowledge of how these parameters may be linked to depositional environments, facies, and diagenetic history of the shale will improve the understanding of pore-to-reservoir scale behavior, and provide improved estimates of prospective CO₂ storage.

Keywords (max 6): Carbon sequestration; storage resource; shale; carbon dioxide.

Highlights (3-5, mandatory):

- The majority of shales will act as seals, but shales that have been hydraulically fractured may serve as CCS reservoirs
- US-DOE-NETL methodology for carbon dioxide storage resource estimation in shale formations
- Intended for national-scale prospective resource estimation and screening

1 Introduction

Anthropogenic carbon dioxide (CO₂) produced by the combustion of fossil fuels can be diverted from the atmosphere into geologic formations through a process known as carbon capture and storage (CCS) (US-DOE-NETL, 2012). Geologic storage of CO₂ in the subsurface has been assessed for deep saline formations, depleted conventional oil and gas reservoirs, and unmineable coal seams (Koide et al., 1992; Harpalani et al., 2006; Bachu et al., 2007; Zhou et al., 2008; Goodman et al., 2011; US-DOE-NETL, 2015). While the majority of shale formations are expected to serve as impermeable seals for stored CO₂, depleted hydrocarbon-bearing shales have also been suggested as potential candidates for future geologic storage of CO₂ (Curtis, 2002; Nuttall et al., 2005; EIA, 2011; Kang et al., 2011; Jarvie, 2012; Liu et al., 2013; Tao and Clarens, 2013; Godec et al., 2013b; Kulga et al., 2014). Hydrocarbon-bearing shales are regionally extensive, underlying approximately 777,000 km² (~10%) of the contiguous United States (Fig. 1), and are currently producing tens of billions of cubic meters (trillions of cubic feet) of natural gas annually.¹ Shale gas accounted for 23% of the total natural gas produced in the United States in 2010 and this percentage is expected to increase to 49% by 2035 (EIA, 2012). Once depleted of natural gas or other hydrocarbons, the pore space and vacant adsorption sites in these rocks are potentially available for storing CO₂.

The aim of this paper is to lay out a methodology, a set of principles and methods, for assessing the prospective CO₂ storage resource in shales. The paper's aim is to present a *methodology*, not a method. By comparison, a method paper has as its aim the determination of specific values for physical parameters and efficiency factors by utilizing physically measured or numerically calculated values. Thus, the aim of this paper is not to establish efficiency terms and apply the resulting method to determine a national-scale CO₂ storage resource, but rather to establish a theoretical basis for future method papers.

¹ For the purposes of this article, we consider hydrocarbon-bearing shale formations to include the complex mixture of lighter hydrocarbons in natural gas and liquids.

Fig. 1: Shale formations in the United States

1.1 Carbon storage in shale: advantages and disadvantages

While the vast majority of shale formations are expected to be impermeable sealing layers for CO₂ storage, a small fraction are expected to undergo the large-scale hydrocarbon production that must precede CO₂ storage in a shale formation. The storage of CO₂ in depleted hydrocarbon-bearing shales may be able to take advantage of existing surface pipeline rights-of-way, well infrastructure, and most importantly, the engineered hydraulic fracture networks created for hydrocarbon production.² Furthermore, the injection of CO₂ into shale reservoirs prior to completion of hydrocarbon production may enhance the recovery of the remaining gas or

² The authors note that this may be a significant assumption as there are no current guidelines available on whether EOR fields will easily convert to dedicated CO₂ storage phase without significant well infrastructure rework, well permitting process, and Area of Review survey requirements. However, the primary advantage is expected to be the existence of a large induced hydraulic fracture network from previous hydrocarbon production.

oil in place, while also maintaining reservoir pressures to avoid the permeability losses associated with pore pressure decline during production (Soeder et al., 1986; Soeder, 1988). In shale, CO₂ preferentially occupies sorption sites with denser sorption packing on organic matter and clays relative to methane (CH₄), the primary component of natural gas (Nuttall et al., 2005; Dilmore et al., 2015). Unlike methane, CO₂ tends to demonstrate multilayer sorption on clay and kerogen that greatly increases the amount of CO₂ stored in a sorptive state (Vermylen, 2011; Jin and Firoozabadi, 2014). As such, CO₂ injected into a partially depleted hydrocarbon-bearing shale could be expected to displace methane from adsorption sites, allowing it to desorb and be recovered (Godec et al., 2013b; Kulga et al., 2014). The potential to use existing wells for CO₂ injection to help recover additional natural gas would offset some of the costs associated with CCS, potentially providing an economic advantage to storage in partially depleted hydrocarbon-bearing shales compared to CCS in deep saline formations (Nuttall et al., 2005; Kang et al., 2011; Wang et al., 2011; Chareonsuppanimit et al., 2012; Godec et al., 2013a; Godec et al., 2013b; Tao and Clarens, 2013; Tayari et al., 2015).

Carbon dioxide may be contained in shale as a free fluid phase within accessible void spaces such as matrix pores and fractures and as an adsorbed component on organic material and clays (Curtis, 2002; Busch et al., 2008; Chalmers et al., 2012; Loucks et al., 2012; Godec et al., 2013b). Storage of CO₂ in the sorbed phase has the added advantage of immobilizing the CO₂ molecules, which may reduce the likelihood of leakage to the surface (Busch et al., 2009).

Cited disadvantages of using depleted hydrocarbon-bearing shales for CO₂ storage relate primarily to the low permeability of these formations. Shales are extremely tight rocks, generally exhibiting matrix permeabilities in the sub-microdarcy (μD) to nanodarcy (nD) range (Soeder, 1988; Liu et al., 2013) (1 darcy=10⁻¹² m²/1.01325). A nanodarcy is a thousand times smaller than a microdarcy (10⁻⁶ darcy), which is the permeability range of most nominally “tight” sandstones and coals (Randolph and Soeder, 1986); it is a million to a billion times smaller than the millidarcy (10⁻³ darcy) to darcy permeabilities typical of conventional oil and gas reservoir rocks. To put this in context, if a depleted millidarcy (mD) conventional limestone or sandstone reservoir can accept one standard cubic meter of CO₂ per second per square meter of exposed wellbore, then under those same conditions a square meter of exposed nD shale wellbore would require a million seconds, or 11.6 days, to accept the same amount of CO₂.

Economical natural gas production from shale is achieved by using induced hydraulic fractures to connect natural formation fractures to the wellbore to create a network of high-permeability flowpaths throughout a large volume of rock. The millidarcy to darcy permeability (Mayerhofer et al., 2006) fractures important to flow in shale can actually be quite small (Soeder, 1988, Table 3), and generally create little void space for storage, typically < 1% of the bulk rock volume (Randolph and Soeder, 1986). Thus, the porosity and organic and mineral component sorption sites in the shale matrix itself represent most of the available storage space. This “dual porosity” nature of shale – fractures for flow and matrix for storage – leads to natural gas production decline curves that show a rapid, initial drop as fractures are drained, followed by a long, slow fall-off of production for many years at much lower rates as gas migrates from the matrix to the fractures and flows to the well (Soeder, 2012). Using hydrocarbon-bearing shale for storage of CO₂ would follow the reverse path, quickly filling the fracture system, followed by the slow uptake of gas into the rock matrix.

In terms of practical carbon dioxide storage applications, the low permeability nature of shales will need to be offset by economic advantages. These include cost savings from detailed, prior site characterization, the ability to utilize existing infrastructure including wells, well pads, and surface pipeline rights of way, and the potential for enhanced hydrocarbon production from CO₂ injection (Tayari et al., 2015). However, the primary advantage is expected to be the existence of a large induced hydraulic fracture network from previous hydrocarbon production.

Examples of the largest currently producing shale formations in the United States include the Marcellus Shale in the Appalachian Basin, the Barnett and Eagle Ford Shales in Texas, and the Niobrara Shale in Colorado and Wyoming. Those shale plays are ideal candidates for the application of the CO₂ storage resource estimation methodology described in this paper. By comparison, hydrocarbon production in the Bakken-Three Forks Play in the Williston Basin comes from a more porous and permeable carbonate-dominated non-shale member sandwiched in between two organic-rich black shales (LeFever et al., 2013). Thus, while the predominantly oil-producing Bakken-Three Forks play made North Dakota the second largest oil producing state in 2014 (EIA, 2014), it would not be a good candidate for the application of this methodology; instead, a more traditional methodology for estimating storage potential (Goodman, 2011; US-DOE-NETL, 2015) or a hybrid methodology may be more appropriate for the Bakken.

1.2 Storage Resource Estimation

The objective of this paper is to present a methodology to quantify the amount of CO₂ that can potentially be stored in shale. The approach is to start with formations in single basins at regional scales, and then combine assessments to produce a national estimate of the prospective CO₂ storage resource in depleted hydrocarbon-bearing shales in the United States. As defined in NETL's Best Practices for Site Screening, Site Selection, and Initial Characterization for Storage of CO₂ in Deep Geologic Formations, prospective storage resources are defined during the exploration phase when potential sub-regions are identified, as analogous to the exploration process applied in the petroleum industry for identifying prospective oil and gas resources (US-DOE-NETL, 2010). Developing a methodology for estimating the storage resource of depleted hydrocarbon-bearing shale builds upon previous work for quantifying the national CO₂ storage resource in conventional oil and gas reservoirs, deep saline formations, and unmineable coal seams (Goodman et al., 2011).

A prospective CO₂ storage resource in the subsurface may be assessed using either a production-based approach or a volumetric approach. Production-based methods use estimates of the ultimate oil and natural gas production from an underground reservoir (known as "estimated ultimate recovery" or EUR) and informed assumptions for the equivalent amount of CO₂ that can be stored in the same formation to determine the prospective CO₂ storage resource, e.g. Tao and Clarens (2013). Uncertainties include the accuracy of estimates for total hydrocarbon production, and the potentially different physical and chemical behaviors of CO₂ and CH₄ in the pore space and on sorption sites. Production-based methods for CO₂ storage in depleted hydrocarbon-bearing shales have merit and provide valuable insights (Tao and Clarens, 2013) but are challenging to use for national-scale assessments of prospective resources that have not yet been produced. Similar to volumetric methods, production-based approaches are associated with a number of uncertainties, particularly in the case of shales. Injecting CO₂ into shale pore space previously occupied by natural gas is not a simple one-to-one replacement. Differences in molecular size, shape, chemistry, packing, and adsorption properties between CH₄ (and other hydrocarbons) and CO₂ result in different behaviors in the shale matrix, with the potential for shale to actually hold more CO₂ than methane (Tao and Clarens, 2013). However, the details of

which factors in the lithology, mineralogy, organic content, thermal maturity, etc. that actually control this behavior are not yet well understood (Lahann et al., 2011). Similar questions have been the focus of laboratory experiments injecting CO₂ into coal (Kutchko et al., 2013). By comparison, the volumetric approach produces a storage resource estimate using the bulk geologic volume of the formation from the mapped area and thickness, the percentage of this bulk volume that is pore space, and informed assumptions regarding processes that will reduce the fraction of pore space that can ultimately be filled with CO₂. Uncertainties in this approach stem from the initial estimate for total rock volume and porosity as well as the estimate of the fraction of that porosity that may be accessible and available for storage of CO₂.

Estimates of fluid volumes in the pores of rock formations have been performed extensively for decades by the oil and gas industry, with distinctions being made between prospective resources, contingent resources, and reserves (Oil and Gas Reserves Committee, 2011; US-DOE-NETL, 2010). Goodman et al. (2011) discuss parallels between national-scale prospecting estimation for hydrocarbons and CO₂ storage. Many of these lessons are relevant to CO₂ storage assessments in depleted hydrocarbon-bearing shales at a national level. In general, national-scale resource assessment differs in data availability and specificity compared to the detailed analysis done for individual reservoirs. When either hydrocarbon or CO₂ storage prospecting are done at the national scale, the work is often performed with limited information, including minimal to no geophysical, well log, or core data. Although some of these datasets may be available for the productive play areas of shales, a nationally-applicable prospecting method must be robust enough to include undeveloped formations with limited data. A requirement of developing a prospective storage resource methodology is broad applicability using information that would reasonably be expected to be available at the earliest project stage, which would include the potential volume of CO₂ storage in hydrocarbon-bearing shales that have not yet been drilled or produced. As such, the methodology developed for shale storage described in this paper is volumetric-based, and consistent with the previous methods and methodologies used to assess the prospective CO₂ storage resources of deep saline formations and unmineable coal seams (Goodman et al., 2011). One significant difference between this shale methodology and those described for other formations is that this methodology assumes, without access to specific reservoir property data, that if a shale is prospective enough for natural gas development to merit drilling and hydraulic fracturing, then it is also prospective for eventual

CO₂ storage. Thus, the very acts of drilling and hydraulic fracturing are considered screening criteria, although the volume of actual production from the shale is not.

The volumetric method of estimation first defines a volume using a total area (A_t) and gross thickness or height (h_g) and the resulting volume is then partitioned into solid and void portions. The basic form of a volumetric-based equation to calculate mass storage potential is therefore:

$$G_{CO_2} = A_t h_g [\phi \rho_{CO_2} + (1 - \phi) \rho_{sCO_2}] \quad (1)$$

where G_{CO_2} is the total possible mass of CO₂ that can be stored in the available volume, ρ_{CO_2} is the density of liquid or supercritical CO₂ at downhole conditions, ρ_{sCO_2} is the mass of CO₂ sorbed per unit volume of solid rock, ϕ is the porosity, and $1 - \phi$ is the solid fraction. The fraction of the total solid and void that can be filled with CO₂ in practice is represented by efficiency factors (E), which range in value from 0 to 1 and represent a fractional reduction in storage volume caused by a combination of practical limitations or physical processes.

This paper seeks to develop a representative prospective storage resource equation for depleted hydrocarbon-bearing shales that incorporates additional terms to address limitations on the potential storage resource of CO₂ in a shale volume. In effect, this volumetric approach begins with the largest functional storage unit – the formation – then reduces it by imposing limits dictated by practicality and physical processes. Defining representative values of those limits is the true technical challenge and will be addressed in future efforts.

2 Geologic properties and production of shale

A review of shale geology is provided to highlight the key attributes of these rock formations and important aspects of how these rocks interact with CO₂. Shale is a fine-grained, clastic rock formed by the deposition of primarily mud-sized sediment particles, which include clay minerals, organic material, detrital quartz, and other components. Mud-sized sediments remain in suspension at fairly low water energies, and require quiet, almost stagnant water before being deposited. The flat, platy clay minerals commonly settle out aligned parallel to bedding, imparting a property known as “fissility” to the rock that allows it to split into paper-thin sheets. To be defined as “shale” in the strict sense of the term, a fine-grained, clastic rock must be fissile, otherwise it is known as a “mudrock.” However, in stratigraphic nomenclature, the term

“shale” is typically applied to an entire formation of fine-grained, clastic sedimentary rock, whether or not all of it is fissile (Soeder, 2012).

Organic-rich shales are characterized as unconventional reservoirs because unlike conventional reservoirs, in which hydrocarbons were concentrated by migrating into a geologic trap from a thermally-mature source rock, the shale itself constitutes the hydrocarbon source, reservoir, and seal. Unconventional resources require hydraulic fracturing or some other form of reservoir stimulation to produce economical amounts of hydrocarbons (Boswell, 1996). Organic-rich shales typically contain a relatively uniform distribution of hydrocarbons throughout the formation, and thus are defined by the USGS as “continuous resources” (Charpentier and Cook, 2011). As such, production well locations are often dictated by the presence of pipelines, compressor stations, or other surface infrastructure, rather than subsurface geologic structure.

Natural gas is stored in shale formations as a free phase within fractures and matrix pores, and adsorbed on organic materials and clay minerals (Soeder, 1988). Sorption can account for 20–85% of the total natural gas content of organic-rich shale formations depending on organic content, kerogen type, reservoir temperature/pressure, and other properties. (Ross and Bustin, 2008). Low-yield, vertical shale gas wells have been produced since the late 1800s, with lifetimes of decades to more than a century as free and desorbed natural gas slowly permeates from matrix pores and sorption sites, flowing through natural and engineered fracture networks to wells (Soeder, 1988; Boswell, 1996; Carter et al., 2011).

The rate at which shale will yield natural gas per unit volume of rock is typically small; therefore, the technical challenge for producing economical quantities of hydrocarbons from these formations is the creation of permeable pathways in contact with a large volume of rock. Fracture permeability is many orders of magnitude higher than matrix permeability in shale, and natural fractures (Fig. 2) can provide flow pathways for natural gas production. Of course, economic flow rates require that matrix permeabilities, while extremely low, are finite.

Fig. 2. Vertical natural fracture faces creating orthogonal joint sets in an outcrop of organic-rich Millboro Shale (Marcellus equivalent), Clover Creek, VA. Photo by Dan Soeder, 2014.

The engineering designs needed to intercept natural fractures in shale with hydraulic fractures were investigated under the DOE Eastern Gas Shales Project, funded between 1975 and 1992, but the results were inconclusive. The breakthrough that led to the current shale gas development boom was achieved by Mitchell Energy in the late 1990s on the Barnett Shale in Texas by applying a combination of horizontal, directional drilling and staged hydraulic fracturing (Soeder, 2012).

Organic matter in shale is in the form of kerogen, typically Type II, although Type I and Type III may also be present (Schmoker, 1980; Slatt and Rodriguez, 2012). Productive hydrocarbon-bearing shales are commonly marginally-mature to mature source rocks. Thermally-mature hydrocarbon-bearing shales typically do not contain a mobile liquid phase such as oil or water (Hill and Nelson, 2000; Curtis, 2002; Bruner and Smosna, 2011; Jarvie, 2012; Clarkson, 2013).

Light hydrocarbon liquids produced with gas from some shales generally reach the surface in the vapor phase, and condense to liquids at the lower temperatures above ground.

These natural gas liquids, known as “condensate,” are associated with lower thermal maturity and Type II kerogen, and are economically important in shales such as the Eagle Ford, Utica, Marcellus and others. Natural gas can also be biogenic in origin in organic-rich shales present at shallow depths, such as the Niobrara Formation in South Dakota (Soeder et al., 2015a).

Shales with a total organic carbon (TOC) content of 2 weight percent or greater are generally dark in color (Hosterman and Whitlow, 1980) and referred to as “black shale.” Most U.S. black shales contain 2–15% TOC (Schmoker, 1980; Jarvie, 2012; Slatt and Rodriguez, 2012; Dillmore et al., 2015). Shales with a TOC content below 2% are collectively referred to as “gray shale,” although the actual colors may be buff, blue, green, or red, as well as gray, depending on the mineral content (Schmoker, 1980; Hill and Nelson, 2000; Bruner and Smosna, 2011; Soeder, 2012; Jarvie, 2012; Slatt and Rodriguez, 2012).

The inorganic mineral content of shale is predominately quartz (>30%), along with clays (~15–50%), carbonate (~5–30%), feldspar (~3–20%) and lesser amounts of pyrite and apatite (Jarvie, 2012; Clarkson, 2013). High thermal maturity shales typically contain non-swelling clays such as illite, kaolinite, and chlorite (Jarvie, 2012). Swelling clays such as smectite that occur in lower thermal maturity shales may contribute significantly to CO₂ sorption potential because these clays readily incorporate CO₂ molecules into their expandable interlayer structures (Busch et al., 2008).

Porosity in organic-rich shales is generally less than 15% (Soeder, 1988), and consists of void spaces within and between the organic matter and mineral components that make up the rock. Matrix pores within organic-rich shale were classified by Loucks et al. (2012) as follows: 1) intergranular/interparticle, 2) intragranular/intraparticle, and 3) intra-kerogen/organic matter. As discussed previously, porosity contributed by fractures is quite low, and >99% of the volume available in shales for CO₂ storage is in pores, the sorptive components lining these pores, or within the solid matrix. Flow is governed by the multiphase fluid flow and capillary processes that control all porous media flow, with the added complication that diffusive and surface transport properties are non-negligible at nD permeabilities. Transport at the pore- and sub-pore scales in shales should therefore be understood as occurring in a physical space containing all the different pore types present in shale with complex conductivities that are the subject of continuing research, see Goral et al., (2015) or Zhang et al., (2015). Currently, flow of CH₄ or CO₂ at the nm and sub- μ m scales cannot be directly imaged, and the complexities of shale pore

geometries and sizes must therefore be visualized from static images such as the ones presented below.

Interparticle pores are voids that are located *between* grain fragments and minerals, such as the spaces between rigid quartz grains and clay platelets. These pores tend to be well-connected, and are more common in shallower, less-compacted shales. Intergranular pore size in sedimentary rocks is usually related to grain size. As a result, the extremely fine-grained nature of shale results in small pores that are challenging to visualize (Rodriguez et al., 2014). Some of the earliest SEM images of what were thought to be shale “pores” were voids created where mineral grains had been plucked from the surface (Soeder et al., 1986). The recently-developed focused ion beam (FIB) milling technique produces an atomically-smooth, cross-sectional surface that can be examined with an SEM to investigate details of the extremely small pore structures in shale (Schieber, 2010; Loucks et al., 2012; Rodriguez et al., 2014). Figure 3 is an example FIB SEM image of the Marcellus Shale showing the complex shape and size distribution of intergranular pores.

Fig. 3: FIB SEM images of intergranular pores in the Marcellus Shale from Greene County, PA: A) secondary electrons; B) backscattered electrons; C) cathodoluminescence; blue color is likely carbonate and red is likely silicon-based (i.e. quartz and clay). Scale bar = 5 microns. Images modified from Rodriguez et al. (2014).

Intraparticle pores are disconnected from the permeable matrix due to their location *within* grain fragments and minerals, such as the voids inside pyrite framboids. Intra-kerogen pores are defined as the pore spaces within organic matter, which are typically interconnected and are most common in thermally mature, methane-bearing shales (Loucks et al., 2012). Matrix pores in shale typically have a size range of 5–20 nanometers (Nelson, 2009), although they can

be smaller. Transmission electron microscopy is required to achieve the ultra-high magnification necessary to image these extremely small pores, as shown in Fig. 4 (Rodriguez et al., 2014).

Fig. 4: Transmission electron microscope image of intraparticle pores in Union Springs Member of Marcellus Shale; note numerous pores tens of nanometers in diameter or smaller. Modified from Rodriguez et al. (2014)

Some schemes, e.g. (Rouquerol et al., 1994) classify shale pores by size, such as macropores (>50 nm), mesopores (2–50 nm), and micropores (< 2 nm). Intra-kerogen pores fall within the micropore range, and total porosities in shale tend to increase with increasing TOC-content and micropore volumes (Ross and Bustin, 2009; Chalmers et al., 2012). The meso- and micropore sizes typically associated with interparticle and intra-kerogen pores are important to the assessment of CO_2 storage potential in organic-rich shales, because these are more likely to be interconnected and accessible to gas (Ross and Bustin, 2009; Loucks et al., 2012). The kinetic diameter of CO_2 is approximately 0.33–0.35 nm, allowing it to enter most shale micropores (Chalmers et al., 2012; Clarkson, 2013).

The depletion of natural gas from a shale gas well, largely regarded as necessary to make room in the subsurface for CO_2 storage, may lead to additional challenges. The reduction in pore pressure due to the extraction of natural gas increases the effective or net confining stress on the rock matrix. A change to high net stress can significantly reduce matrix permeabilities (Randolph and Soeder, 1986). All pore types appear to stay open to some degree under subsurface pressures associated with depths up to 4569 m or 15,000 feet (Loucks et al., 2012). However, low

permeability rocks, especially those with slot-like or flat pore structures like shale and coal tend to be especially sensitive to high net stress excursions (Randolph and Soeder, 1986).

The responses of shale matrix pores and flowpaths to increases in net confining stress during drawdown under natural gas production are not well understood. Laboratory data indicate that shales are sensitive to high stress: e.g., doubling net confining stress can result in a 70% reduction in matrix permeability (Soeder, 1988). Slope changes on the Klinkenberg plot indicate that the median pore size in the matrix actually increases under elevated net stress, which has been interpreted to mean that the smaller pores are more readily compressed and closed off under high net stress (Soeder et al., 1986). This loss of smaller pore sizes is accompanied by an increase in flowpath tortuosity, indicating a related reduction in flowpath inter-connectivity. Laboratory experiments show significant hysteresis in shale. As displayed in Fig. 5, reducing the stress on the rock after a high net stress excursion did not restore the original permeability within the time frame of the laboratory experiment (Dilmore et al., 2015). This is probably due to the crushing of the asperities that prop open the flat or slot-like pores (Randolph and Soeder, 1986).

Fig. 5. A series of dry nitrogen gas permeability measurements on a sample of Marcellus Shale during a high net stress excursion. The upper black line shows permeability decreasing to the right as net confining stress increases, and the lower blue line shows permeability increasing back toward the left as net stress is later reduced. Data from Dilmore et al. (2015).

Results from simulations suggest that permeability hysteresis after an excursion to high net stress will not significantly impact the CO₂ storage potential (or enhanced gas recovery) in

very low permeability shales (Kulga et al., 2014). Getting CH₄ or CO₂ to move in or out of these rocks is already so difficult that reducing the permeability further through an excursion to high net stress is likely to make little difference. However, additional experiments are needed to help better define the net stress responses of shale and potentially develop a specific reservoir pressure management strategy for stress control on shale gas wells that are intended to be used later for CO₂ storage.

In addition to matrix permeability reduction with increasing net stress, propped and unpropped fracture permeability also decreases with increasing net stress (Schubarth et al., 1997; Miller et al., 2011; Ahn et al., 2014). Because fractures represent an important pathway for the movement of fluid through shales, this represents a significant potential source of injectivity and effective storativity reduction. Again, however, injection of fluid will decrease net stress and likely restore or partially restore fracture permeability lost due to pressure drawdown during primary production.

3 Previous CO₂-shale storage resource and capacity estimates

Methods have been developed to estimate the CO₂ storage potential of shale based on CO₂ sorption isotherms, geologic and volumetric data, and assessments of gas-in-place (GIP) and estimated ultimate recovery (EUR) of shale gas (Nuttall et al., 2005; Godec et al., 2013a; Godec et al., 2013b; Liu et al., 2013; Tao and Clarens, 2013, Edwards et al, 2015). These methods have mostly been applied to U.S. organic-rich shale formations in the Illinois and Appalachian Basins (Nuttall et al., 2005; Godec et al., 2013b; Tao and Clarens, 2013), likely due to significant regional power plant CO₂ emissions and the proximity of active shale gas production.

Nuttall et al., (2005) estimated ~28 Gigatonnes (Gt) of CO₂ can be stored in the deepest (≥ 304 m or 1,000 ft.) and thickest (≥ 15 m or 50 ft.) portions of the Ohio Shale and New Albany Shale. Godec et al. (2013b) estimated the CO₂ storage potentials of the Marcellus Shale at depths greater than 915 m (3,000 feet) to be 99 Gt of adsorbed gas and 72 Gt of free gas for a theoretical maximum of 171 Gt, although the technically-accessible CO₂ storage is estimated at a much lower 55 Gt. Tao and Clarens, (2013) developed a production-based model to estimate theoretical CO₂ storage potential in shales using the ratio of CO₂:CH₄ sorption and diffusivities,

and reported 10.4–18.4 Gt of CO₂ could be stored in the Marcellus Shale by 2030. Godec et al. (2013a) estimated the technically accessible CO₂ storage potential for organic-rich shale formations globally based on estimates of GIP and EUR reported by the U.S. Energy Information Administration in 2011 (EIA, 2011). They reported a CO₂ storage potential of about 740 Gt of CO₂ in 69 gas shale formations in 32 countries, of which 134 Gt are in 19 shale formations in the United States.

Sorption was the primary mechanism for CO₂ storage in shale that was examined and considered in many of these studies (Nuttall et al., 2005; Busch et al., 2008; Chareonsuppanimit et al., 2012; Liu et al., 2013; Tao and Clarens, 2013). Experimental analysis of CO₂ sorption trends in shale samples, studies of CO₂-shale interactions, and reservoir simulations have been used to investigate the mechanisms and potential for CO₂ storage in shale (e.g. Busch et al., 2008; Lahann et al., 2011; Chareonsuppanimit et al., 2012; Liu et al., 2013). These studies have established the importance of TOC content for the presence of CO₂ adsorption potential in organic-rich shales, while showing that factors other than TOC, such as clay mineralogy may also contribute (Chareonsuppanimit et al., 2012). For example, Busch et al. (2008) reported significant CO₂ storage potential in the Muderong Shale in Australia, despite low TOC content (<0.5% by weight). This suggests that CO₂ sorption on some types of clay may be an important factor for CO₂ storage, serving the same sorptive function as high TOC in some shale formations. If this is also the case for shale formations elsewhere, organic-lean, gray shale may be a potential CO₂ storage resource, depending on clay type and abundance.

In addition to adsorbed gas, an estimated 15–80% of methane in organic-rich shale occurs as a free gas phase in matrix pores and fractures (Lewis et al., 2004; Ross and Bustin, 2008). As such, CO₂ storage in shale pore space as free gas is also important to consider in an assessment.

4 US-DOE-NETL methodology for estimating CO₂ storage resources in shale

The US-DOE National Energy Technology Laboratory has provided a variety of estimates for prospective CO₂ storage resources in the subsurface at national and regional scales for the United States and parts of Canada since 2007 (US-DOE-NETL, 2012). As such, a screening-level approach has been developed for use in producing meaningful assessments with the limited data available at the earliest project stages, prior to the onset of site-specific

measurements in the subsurface. Previous methods and methodologies have been developed for CO₂ resource estimation in deep saline formations, depleted conventional oil and gas reservoirs, and unmineable coal seams (Goodman et al., 2011). The US-DOE-NETL approach defines a *storage resource estimate* as the volume of underground space that can be accessed for prospective CO₂ storage (US-DOE-NETL, 2010). A *storage capacity estimate* considers detailed geologic properties and also includes legal, regulatory, and economic limitations (US-DOE-NETL, 2012).

The US-DOE-NETL approach for assessing the prospective CO₂ storage resource of shale relies on limited information and relatively simple statistical tools to estimate the fraction of a body of rock that will be available for CO₂ storage based on a volumetric equation (US-DOE-NETL, 2010, 2012). The use of such a methodology for estimating the prospective CO₂ storage resource in deep, saline formations has been shown to be statistically indistinguishable from other, more detailed methodologies and methods, with uncertainties in geologic data causing larger differences in storage estimate results than the choice of storage estimation method (Goodman et al., 2013).

The US-DOE-NETL volumetric methodology for assessing prospective CO₂ storage was developed to provide a framework for a future method meeting three important requirements:

1. The method must be stochastic, rather than deterministically predictive, and the estimated potential for subsurface storage of CO₂ based on representative parameter values that are applicable to all formations in the United States, not just those with available geophysical or production datasets.
2. The method must be capable of being applied by external stakeholders, e.g. other government entities and future project developers, to support high-level decision-making related to subsurface carbon storage.
3. A uniform method is required for the U.S. Department of Energy's Regional Carbon Sequestration Partnerships (RCSPs) to generate a consistent and comprehensive national storage resource estimate.

4.1 Criteria for shales usable for storage

A volumetric analysis for the estimation of CO₂ storage resources in shale must first determine suitability criteria for shale formations. The vast majority of shale formations are expected to be impermeable sealing layers that act as caprocks, e.g. seals for CO₂ storage, while only a small fraction are expected to undergo the large-scale hydrocarbon production that must precede CO₂ storage in a shale formation.

As a first screening criterion, shales targeted for prospective storage are those formations where hydrocarbons have been, or are expected to be, commercially produced through stimulated fracture networks. Large-scale commercial shale hydrocarbon development is a requirement because it leaves behind subsurface infrastructure including (generally) long horizontal wells and high-volume hydraulic fracture networks that provide access to large volumes of shale. Hydrocarbon production also removes significant amounts of methane from the rock, creating more underground space for storing CO₂. It is also likely that commercial shale development sites will have detailed site characterization and production data available for accurate, predictive field- and well-scale reservoir modeling. The decline curves or production history of commercial gas wells will provide documentation that the hydraulic fracture networks are sufficiently connected and efficient for transport. The majority of these formations are organic-rich black shales in major gas plays like the Barnett or Marcellus; a high organic content is a screening criterion for commercial gas development, though not a strict requirement for CO₂ storage. In summary, by requiring that shales for storage have already been produced, they will possess favorable fracture transport properties, existing infrastructure and site data, and available pore space and sorption sites as a result of prior or current fluid displacement.

While all shales that are currently being produced satisfy this criterion, there are a number of shales that have geologic characteristics similar to currently-producing shales, but have not yet produced hydrocarbons. For the resource estimation methodology to be inclusive and forward-looking, all prospective shales must be considered. A good example of this would be the Utica Shale, which began production a number of years after the Marcellus boom. The pre-development Utica would have satisfied this storage criterion, because the formation was known to have resources similar to the Marcellus, even though it had not yet been produced.

It should be noted that the majority of shale formations in the United States will not satisfy this criterion. Many of these have sparse geophysical or prospecting data and cannot be considered a prospective storage resource unless there is some indication that the rock is suitable

for the commercial-scale hydrocarbon production that must precede CO₂ storage in a shale. Similarly, many shales are identified on geologic maps as being too shallow or too thin for production, and also would not fit this criterion. Even some currently-producing shales will not satisfy this criterion. For example, vertical shale gas wells in the gray Chagrin Shale in northeast Ohio have been producing small amounts of gas on farms for non-commercial use since the 1870s (Hoover, 1960). However, the Chagrin has not undergone the large-scale, staged hydraulic fracturing needed to create the necessary subsurface infrastructure for storage, and the low production rates indicate that the existing wells lack connection to the large volumes of rock necessary for CO₂ storage in shales. Most organic-lean gray shales like the Chagrin are not likely to have generated sufficient methane to produce the gas overpressures that are thought to have contributed to the development of natural fractures (Engelder, 2009). Figure 6 shows gray shale predominating in a Devonian cross-section through the Appalachian Basin (Potter et al., 1980).

The second screening criterion for storage in shale formations is a minimum depth of 800 meters (~2500 ft.) needed to obtain sufficient hydrostatic pressures to ensure CO₂ is in a dense liquid or supercritical state. CO₂ in the liquid or supercritical phase stores more efficiently than gas.

The third criterion is the presence of a suitable seal to prevent the vertical migration of CO₂ to overlying formations or aquifers. Because hydrocarbon producing shales have been fractured, suitable storage shales require a redundant independent overlying seal. A subset of shale formations meant for CO₂ storage may be sufficiently thick (100s–1000s of meters) for their upper layers to remain unfractured and intact and to act as sealing layers for the lower layers.

Table 1. Requirements for CO₂ storage in shale formations

Criteria for CO₂ Storage in Shale Formations
1) Hydrocarbons have been or expect to be commercially produced from the shale through stimulated fracture networks.
2) The prospective shale formation (or portion thereof) being assessed must exist at pressure and temperature conditions adequate to keep the CO ₂ in a dense state, either liquid or supercritical (>800m).

3) A suitable seal system must be in place to prevent the vertical migration of CO₂ to the surface.

Fig. 6. Vertical cross-section of the Appalachian Basin from Ohio into Pennsylvania (see inset map for location) showing the layered sequence of Devonian-age black (black color) and gray shales (gray color) , and coarser sandstones (stippled) in the east. The Marcellus Shale is at the bottom. Note the significantly thicker gray shales compared to the relatively thin black shales. Modified from Potter et al. (1980).

4.2 Volumetric Equation

A volumetric-based, CO₂ prospective storage resource equation for shale was defined in the Introduction section by Eqn. 1, which separates the storage space into free gas storage and sorbed storage. When taking efficiencies of storage into account, Eqn. 1 becomes:

$$G_{CO_2} = A_t E_A h_g E_h [\rho_{CO_2} \phi E_\phi + \rho_{sCO_2} (1 - \phi) E_S], \quad (2)$$

where G_{CO_2} is the mass of CO₂ that is stored in the available volume, and E_A , E_h , E_ϕ , and E_S are efficiency factors for the area, thickness, pore volume, and sorbed volume, respectively. There is a great deal of uncertainty inherent in the parameters of the equation, especially the efficiency factors, due to significant complexities involved in several of the fundamental processes associated with production, injection, and storage within shales. Despite the uncertainties, the equation works as an approach to a methodology. As data are added over time to reduce the uncertainties, the utility of derived methods will improve, but the purpose for developing these equations is simply to establish the basic methodology.

To understand how the CO₂ is stored within shale, first consider how methane is stored and produced. Initially, methane is found as both a free phase gas in the pore space within the shale and as molecules sorbed to the solid shale matrix. Free gas is initially located within naturally-existing conductive fractures in the shales and within pores in the shale matrix. Because of the very low permeabilities in most shales, typically nD, the gas is difficult to remove. Once a horizontal well is drilled and hydraulic fracturing takes place, a conduit is created between the location of the gas in the formation and the production well. Generally, the free gas has to follow a very tortuous pathway to get from inside of the shale to the production well, driven by a pressure and concentration gradient: 1) the gas diffuses through pores within the shale matrix to an existing natural fracture, 2) it flows through the natural fracture towards an induced fracture, and 3) the gas flows through the induced fracture to the production well. Depending on the location of the gas molecule, it may flow directly from a pore or the matrix through fractures to the well, or it may originate in the natural fracture. The path for sorbed gas is similar, but it begins by desorbing from the matrix rock before entering the free gas phase. This is similar to the process by which methane is produced from coal: desorption from the matrix, diffusion through the matrix, and advection through existing fractures (Remner, 1984). Similarly, gas adsorption to carbon in the shale matrix may cause swelling-induced permeability reductions

that are similar to what occur in coal. One of the main differences between shale and coal is that the cleat systems in coals are often spaced centimeters or less from each other so that the majority of the coal will eventually be depressurized during production of coalbed methane, while natural fracture spacing in shales may vary widely such that hydraulic fractures are necessary to contact enough of the shale surface to justify production. Thus, large, disconnected portions of the shale formation may never be depressurized during production, and thereby are not produced and not accessible to CO₂ storage. Because of the low permeability of the shale matrix and the often disconnected natural fracture system in most shales, production recovery efficiencies are often quite low, on average 25% over the lifetime of an average U.S. shale well (Godec et al., 2013b). Challenges with desorbing gas, especially if abnormally low reservoir pressures are required, may also be a contributing factor to low recovery efficiencies (Chareonsuppanimit et al., 2012; Zhang et al., 2012).

The process of CO₂ storage uses the same pathways in the rock as the process of production, only in reverse, with the CO₂ beginning at the injection well, flowing through hydraulic fractures and eventually to sorption sites or pore space within the matrix rock. From the wellbore, CO₂ enters an artificially-induced fracture network. The hydraulic fractures are directly connected to the wellbore, held open with a relatively-coarse, high-permeability, proppant sand, and likely have larger fracture apertures and lower capillary entry pressures compared to the natural fracture network. The natural fracture network extends throughout the targeted reservoir and is the primary conduit to connect the wellbore and artificial fracture network to the nD-permeability matrix pore volume, i.e. it controls the well-scale sweep efficiency. Furthermore, natural fracture apertures are heterogeneous and finite differences in capillary entry pressures and thus multiphase occupancy will cause fluid bypass. The volume of pore space that can be filled with CO₂ is therefore substantially less than 100% because a portion of the CO₂ will never reach the pore space due to transport heterogeneities associated with fracture networks and low matrix permeability. After traveling through the artificial and natural fracture networks, CO₂ reaches the nD permeability shale matrix, where transport is nearly diffusive and CO₂ movement into the matrix occurs over decadal time scales. For carbon storage, it is assumed that these complex pathways will similarly provide low storage efficiencies. The efficiency parameters are meant to take all of this complexity into account.

If only a subset of a shale formation meets the necessary criteria for CO₂ storage, then properties of that subset of the formation should be used to determine parameter and efficiency values rather than data from the entire formation. For example, if one part of a formation does not have a well-developed natural fracture network it will provide no effective carbon storage potential and E_A or E_h will be reduced accordingly. As such, void and sorbed parameter and efficiency factor values in Eqn. 2 (ϕ , E_ϕ , E_S , ρ_{CO_2} , and ρ_{sCO_2}), should not reflect the excluded region. Rather, their values and related uncertainties should represent only the subset of the formation geology and wells in the effective formation volume (V_e):

$$V_e = A_t E_A h_g E_h. \quad (3)$$

In other words, the well- or pore-scale efficiencies in Eqn. 2, should be representative of only the prospective portion of the shale formation whose volume is defined by V_e .

Additionally, it should be pointed out that the efficiency factor for the sorbed gas, E_S , is a combination of the efficiency of the volume of matrix rock contacted by gas (E_m), i.e. reductions due to transport processes, and the efficiency of sorptive packing of gas at reservoir conditions (E_{sorb}). Thus, $E_S = E_m E_{sorb}$. With this substitution, Eqn. 2 becomes:

$$G_{CO_2} = A_t E_A h_g E_h [\rho_{CO_2} \phi E_\phi + \rho_{sCO_2} (1 - \phi) E_m E_{sorb}]. \quad (4)$$

4.3 Parameter Definitions and Measurement

Detailed definitions and explanations of both the physical parameters and efficiency factors for Equations (2) – (4) are provided in Tables [4-2](#) and [23](#). Descriptions of the methods that can be used to determine values for each term are included in the narrative that follows. The presentation of physical parameter and efficiency terms in the tables is organized by decreasing scale, narrowing from basin-scale processes to pore-scale processes such as clay and kerogen sorption.

Table 4-2: Definitions of physical parameters in the CO₂ storage equation (Equation 4)

G_{CO_2}	CO ₂ storage resource (mass) of the shale formation
A_t	Total area (map view) of the shale formation being assessed for CO ₂ storage

h_g	Average gross thickness of the shale formation
V_e	Net effective volume of the formation ($A_t E_A h_g E_h$)
ρ_{CO_2}	Density of CO ₂ at the average pressure ($\bar{P}$) and temperature ($\bar{T}$) of V_e prior to gas production
ρ_{sCO_2}	Maximum mass of CO ₂ sorbed per unit volume solid rock, e.g. the asymptotic value of an appropriate isotherm

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625 | **Table 23:** Definitions of the efficiency factors in the CO₂ storage equation (Equation 4)

E_A	Fraction of shale formation total area available for CO ₂ storage
E_h	Fraction of shale formation gross thickness available for CO ₂ storage
E_ϕ	Fraction of shale porosity within the net effective volume of the formation, V_e , available for CO ₂ storage. This is a reservoir scale efficiency factor that is meant to address the probability that CO ₂ will never reach some of the pore space due to transport heterogeneities associated with fracture networks and low matrix permeability.
E_S	Fraction of the total potential sorbed volume of CO ₂ within the net effective volume of the formation, V_e , ($E_m E_{sorb}$). This is a reservoir scale efficiency factor that is meant to address both transport and sorption inefficiencies.
E_m	Fraction of the shale matrix within the effective volume of the formation, V_e , available for CO ₂ storage. This is a reservoir scale efficiency factor that is meant to address the probability that CO ₂ will never reach some of the shale matrix rock due to transport heterogeneities associated with fracture networks and low matrix permeability.
E_{sorb}	Fraction of ρ_{sCO_2} due to reductions in sorptive packing at reservoir pressure and temperature conditions. This is a reservoir scale efficiency factor that is meant to address the inefficiency of sorptive packing on shale matrix rock due to competitive sorption (sorption/desorption with other species) and non-ideality of sorption

	surfaces (reduction of surface coverage) in the shale matrix.
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The **formation area** efficiency factor (E_A) represents a reduction in the available storage resource area as shown on a map view of the shale after eliminating acreage due to social or physical restrictions as defined by a regional proximity analysis and social data analysis (US-DOE-NETL, 2010). This assessment identifies and describes locations that are unsuitable for storage, and subtracts them from the total land area underlain by the shale formation. Socially unsuitable storage locations include sensitive areas such as government facilities or national parks, and areas with restrictions such as population centers or land areas in an adjacent state that may have a moratorium on hydraulic fracturing. Social restrictions may change over time, for example the closure of a military base that may consequently open up that land to drilling.

Physical restrictions on locations are somewhat more permanent. These may include areas of the formation that are too shallow for supercritical or liquid CO₂ or too deep to drill. Geological facies changes in a formation can also limit the availability of total shale land area for CO₂ storage. For example, if an organic-rich shale grades laterally into an organic-lean zone, the lean part of the formation may never be drilled and would not be considered a prospective resource. Fig. 7 illustrates several examples of both physical and social restrictions.

Finally, as a practical matter, geological formations typically extend across multiple counties and many times several states, while individual wells contact a comparatively small area. Even with the infill drilling and step-out drilling typical for full shale gas development, 100% of the total available formation area will likely not be drilled and the formation area efficiency will be reduced accordingly.

The **formation thickness** efficiency factor (E_h) represents limits placed on the shale storage resource due to formation-scale characteristics that change as a function of depth. This efficiency is largely driven by changes in the geological properties of the formation in the vertical direction, such as lithology, permeability, porosity, fracture density, fracture connectivity, etc. that are less advantageous for oil and gas production, and as a consequence effectively preclude later CO₂ injection. In saline reservoirs this term addresses stratigraphic porosity and permeability heterogeneities. In shales, reductions in the net to total thickness are more likely to be due to limitations in hydraulic fracture heights, the presence or absence of fracture barriers, and the nature of the rock units that overlie and underlie the target formation.

Fig. 8 provides an illustration of a scenario in which the shale unit underlying a fracture barrier has not been contacted by the hydraulic fractures and is therefore unavailable as a CO₂ storage resource. Recall from Table 1 that the presence of a stimulated fracture network connected to a wellbore is one of the three critical criteria required for CO₂ storage in shale.

Fig. 7: Prospective shale formation (purple) areal efficiency is decreased from unity (i.e. 100%) by a variety of legal/social, physical, and practical limitations. Examples of each are shown on a fictional map for illustrative purposes, e.g. a state with a moratorium on shale development is shown at the top right while a deep lake without any shale gas development is shown at the lower left. The inset shows practical limitations due to incomplete pad-scale areal coverage.

Determination of the net effective volume of a shale formation (V_e) — i.e. the area, thickness, and their respective efficiency factors — for prospective CO₂ storage resource assessment occurs at the earliest prospecting stage. It therefore requires collecting publicly-available geological and social data. Fossil energy resource assessment data, geological maps, and cross-sections such as the ones published by the U.S. Geological Survey can provide initial basic information. For typical references, see (Coleman et al., 2011; Milici et al., 2012; Milici and Swezey, 2006; Ryder et al., 1992; Ryder et al., 2014; Ryder et al., 2012).

Fig. 8: Reservoir engineering in shale formations: low permeabilities require infrastructure to contact a large fraction of the pore space volume; each well pad (top) can have several wells, each having horizontal sections with many stages of multi-cluster hydraulic fracturing (shown schematically as simplified vertical planes oriented orthogonally to well horizontal sections). Also shown (bottom, in red) is an underlying interval of the same formation with properties not amenable to economic hydrocarbon production; that interval has not been targeted for hydraulic fracturing, and because of this is considered unfavorable for CCS. In the CO₂ storage resource assessment methodology presented herein, that reduction in overall storage efficiency would be represented by reducing E_h .

Well-scale parameters and efficiency factors must be representative of the subset of the formation defined by V_e . That is, once the effective storage volume has been reduced by removing less favorable areal regions and sub-strata through the efficiency factors used to calculate V_e , the properties of the remaining volume should be used in Equations (2) and (4). For example, if natural gas cannot be produced from a particular shale facies due to low organic carbon content, this facies should not be included in a calculation of the average kerogen content for the entire formation. The kerogen content of the effective volume (V_e) that meets the criteria of the prospective resource should be used instead.

The transport of CO₂ into the shale from an injection well will proceed through connections among three physical pathways: artificially-induced fractures, natural fractures, and

matrix pores, with two primary types of sorptive surfaces: clays and kerogen. Fig. 9 is a representation of the process. Efficiency terms at the well scale are related to reductions in the available resource due to petrophysical transport limitations. These reductions are caused by a variety of fluid transport phenomena, including: (1) limited CO₂ transport due to finite permeabilities in the fracture networks and nD permeabilities in the shale matrix, (2) the presence of another fluid resulting in reduced relative permeability of CO₂ as well as reduced maximum potential CO₂ saturation, (3) heterogeneity-induced preferential pathways leading to fluid bypass, (4) mass transport limitations reducing CO₂ transport to non-pore surface clay and kerogen, and (5) mass transport limitations reducing CH₄ desorption and thus clay and kerogen site availability for CO₂ adsorption. Additional reductions are caused by limitations on sorption due to pressure and temperature conditions relative to a theoretical maximum sorption per unit rock.

Uncertainties associated with representative physical parameters in shale can be addressed in part with laboratory measurements, while others may require models and assumptions to represent complex, inter-coupled geosystems. Physical properties that can be directly measured in the laboratory include CO₂ densities (ρ_{CO_2}), theoretical maximum CO₂ sorption constants (ρ_{sCO_2}), and porosity. For example, an isotherm representative of the pressure-sorption relationship can aid in establishing ρ_{sCO_2} and the sorption efficiency, E_{sorb} , would be the amount of gas sorbed in V_e at the pressure and temperature conditions of the formation divided by the isotherm volume constant. When creating a particular method based on this methodology, it can naturally be foreseen that researchers will consider relating ρ_{sCO_2} to the total organic content of the shale matrix. Porosity in both hydraulic and natural fracture systems can be assessed using numerical models to represent fracture geometries (Boyle et al., 2014), which may be constrained by production data or field tests.

Fig. 9: Injected CO₂ (purple shading) moves out from the wellbore – driven primarily by pressure gradient – and through a complex network of natural and hydraulic fractures (depicted in this simplified illustration as transverse engineered fractures imposed into a more extensive network of natural fractures) and into the adjacent shale matrix. Storage efficiencies in the volume near the wellbore and hydraulic fractures can be expected to be significantly higher than those far from the wellbore.

A variety of choices for pressure and temperature (P-T) conditions for physical parameters can be considered as being representative of reservoir conditions, e.g.: initial conditions prior to gas production, conditions at either the start or the end of CO₂ injection, conditions required to avoid additional fracturing of the shale formation or fracturing the overlying caprock, etc. Variations in physical parameter values due to the choice of P-T conditions are generally less than the uncertainty associated with limitations in geological data availability at this stage; more importantly, the methodology requires consistency in choice of P-T conditions. Shale formations will have complex pressure-temperature histories during gas production and subsequent CO₂ injection. Predictions, e.g. of post-production or post-injection conditions, require complex reservoir modeling that incorporates various physical and operational data that are not available at the prospecting stage. The only conditions that are both available at the prospecting stage and can be expected to be reasonably representative of conditions over geological time scales are the initial conditions prior to gas production. Therefore, for consistency, we recommend that all physical properties should be calculated at the average reservoir pressure and temperature prior to natural gas production.

The US-DOE-NETL volumetric methodologies and methods for CO₂ storage resource assessment use a log-odds statistical approach; details of this approach and the motivation for its choice as applied to deep, saline formations and unmineable coal seams were presented in Goodman et al. (2011). In brief, storage efficiency is calculated by assigning 10% and 90% probability values to each efficiency parameter in Equations 2–4 [Error! Reference source not found.](#) These specific efficiency values can be calculated by simulation of CO₂ storage under a variety of plausible conditions and variable shale properties, by expert elicitation, or by the collection of field data. The efficiency equations are then calculated stochastically using a Monte Carlo simulation with a log-odds normal distribution for each parameter. At the prospective scale, storage efficiency terms are treated independently and are assumed to be uncorrelated.

5 Discussion

The vast majority of shale formations are expected to be impermeable sealing layers that act as caprocks for CO₂ storage, while only a small fraction are expected to undergo the large-scale hydrocarbon production that must precede CO₂ storage in a shale formation. A rough order-of-magnitude estimate of the formation-scale efficiency for CO₂ storage in shale can be made by analogy to the formation-scale efficiency of natural gas production. The estimated ultimate recovery (EUR) of a gas resource is often expressed as a recovery factor, which indicates the percentage of the total gas-in-place (GIP) that can be produced from a reservoir. An average recovery factor of 25% is projected for hydrocarbon-bearing shales in the United States (Godec et al., 2013b). Recovery factors of 10% and 25% have been published for the Marcellus Shale in the Appalachian Basin (Engelder and Lash, 2008; Godec et al., 2013b) and 8% and 12% for the Barnett Shale in the Ft. Worth Basin (Lewis et al., 2004; Engelder and Lash, 2008).

Studies at the reservoir scale are needed to provide assessments of sweep efficiency, with a particular need for sensitivity analyses of geologic parameters such as depth, thickness, porosity, TOC, matrix permeability, clay and kerogen sorption, thermal maturity, and natural fracture conductivity and spacing (Liu et al., 2013). A number of challenges must be recognized when considering the storage of CO₂ in shales. Shales are heterogeneous, with geologic properties that may vary significantly within and between formations, complicating the analysis of CO₂ storage (Clarkson, 2013). Complex special cases may not be amenable to the purposefully-simple methodology proposed here. Limitations to assessing the prospective CO₂ storage resource in depleted hydrocarbon-bearing shales include the numerous uncertainties associated with each geological and petrophysical parameter, and a related lack of pertinent data, making it difficult to assign appropriate values. In particular, the pore geometry, flowpath interconnectivity, matrix permeability, and stress sensitivity are challenging to quantify (Soeder, 1988; Lahann et al., 2011; Chalmers et al., 2012; Clarkson, 2013; Ruppert et al., 2013). Shale typically contains a dual porosity system of high-permeability, low volume fractures that extend through a porous rock matrix that has extremely low permeability. The matrix permeability can be less than one nD, which greatly inhibits the movement of CO₂ from the fracture system into the matrix (Liu et al., 2013). This is further complicated by sorption-related transport (Singh et al. 2014, Singh and Javadpour, 2015). The impact of hydraulic fracturing and the presence of

water in the shale matrix pores on the production of methane and subsequent storage of CO₂ is poorly understood. Geochemical reactions between CO₂ and shale are also not well understood, nor are the potential impacts on permeability and porosity that may result from mineral precipitation or dissolution, or the extent of swelling for CO₂ adsorbed on kerogen and clays. Storage efficiency of CO₂ in shale is likely to be controlled by induced and natural fracture density, fracture spacing, and flowpath interconnectivity, as well as matrix properties.

Field tests injecting CO₂ into depleted shale wells can help answer some of these questions. Recently, small-scale injection/recovery tests known as "huff and puffs" have been performed on a few shale gas wells, including the successful injection of 509 tons of CO₂ over a thirteen-day period into a Chattanooga Shale well in Tennessee (Louk, et al, 2014). The well used for this test was on production and shut-in while the test was run, and was returned to production afterward. Additional field tests are needed on a variety of wells completed to different depths in different hydrocarbon-bearing shales, and in various stages of depletion.

NETL has a variety of ongoing efforts to collect physical data for efficiency factor determination focused around two different but related approaches (Soeder et al., 2015b). Downhole petrophysical data from wireline well logs are being assessed for the Marcellus Shale in several areas of interest in the Appalachian Basin. These data are being used to refine formation thicknesses and to determine bulk porosity, organic content, and other physical parameters. The second approach is to utilize a high-precision, steady state core analysis device to collect measurements on shale whole core samples. Measurements will include gas permeability, gas porosity, adsorption isotherms for methane and carbon dioxide, pore volume compressibility, and other petrophysical properties under net stress representative of drawdown conditions. These measurements are not intended to assess the reservoir properties of shale in a single well, but rather to understand the broader relationships between petrophysical responses and shale pore structures. Correlations of CO₂ sorption with TOC, thermal maturity, kerogen type and other factors may help show the relative importance of the parameters that influence CO₂ storage properties of shale. Linking the core analysis data to well logs will anchor the well log response to a set of lab data, and allow the use of logs to reduce uncertainty in petrophysical properties across a wide area of the shale play.

The availability of fresh hydrocarbon-bearing shale core material has been extremely limited for public research purposes, and even when access is provided, there is an inherent

concern over possible sampling bias. Samples selected for petrophysical analysis are generally solid, unfractured rock plugs from intact drill cores. Quartz-rich and carbonate-containing shales are typically better indurated and more cohesive than clay-rich samples, which tend to be friable and fissile. These desirable physical properties may result in an under-representation of clay-rich shales in core analysis, leading to biased estimates of matrix porosity, permeability, and CO₂ sorption. Additional uncertainty stems from differences between cores sampled prior to hydraulic fracturing and years or decades of hydrocarbon production and the state of the reservoir rock during post-production CO₂ injection.

Nevertheless, core analysis is critical to determine if the permeability of a depleted gas shale is permanently reduced by hysteresis after an excursion to high net stress. Such investigations may help to define reservoir pressure management strategies that will allow repressurization of shale by CO₂ injection. Other relevant core analysis studies include geochemical reactions between CO₂ and shale, particularly organic materials that may alter the pore structure, creating a potential for localized increases or decreases in permeability and porosity, and measurements of the effects of swelling from CO₂ sorption on kerogen and clays in organic-rich shales. The amount of irreducible water saturation in shale pores and how it may affect the movement and chemistry of CO₂ in the matrix can also be studied.

Despite the unknowns, hydrocarbon-bearing shales possess a number of characteristics that are advantageous for the effective storage of CO₂. Unlike deep, saline formations, depleted hydrocarbon-bearing shales will contain an infrastructure of wells, pipeline rights of way, and engineered fracture systems that could be utilized for CO₂ injection and storage. It may even be desirable to begin injecting CO₂ into a hydrocarbon-bearing shale during the production phase for reservoir pressure management and to facilitate enhanced natural gas recovery (Nuttall et al., 2005; Kang et al., 2011; Wang et al., 2011; Chareonsuppanimit et al., 2012). Adsorbed CH₄ that could not be extracted during primary production could be desorbed by injecting CO₂ and produced to help offset storage costs (Godec et al., 2013b), though this may be tempered if producers are concerned that the potential need to separate CO₂ will be cost prohibitive. Shale formations underlie large land areas of the United States, representing a significant potential CO₂ storage resource (refer back to Fig. 1). CO₂ can be stored in shale in a manner similar to natural gas: as a free phase in void space within fractures and matrix pores, and adsorbed onto kerogen and clays (Curtis, 2002; Chalmers et al., 2012). For economic reasons, horizontal drilling and

hydraulic fracturing operations on hydrocarbon-bearing shales are designed to be limited to the productive target zone within the play area (Fisher and Warpinski, 2012). This helps limit the potential pathways for vertical migration of CO₂ to the surface. Hydrocarbon-bearing shales are commonly overlain by caprocks composed of low-permeability lithologies like dense limestone or gray shale that could act as a primary or secondary seal (Curtis, 2002; Slatt and Rodriguez, 2012). Shale formations considered as a prospective CO₂ storage resource must have a redundant sealing caprock layer, which would serve to mitigate the primary concern with storage of CO₂ in fractured shales: the fractures themselves. However, the requirement of an independent sealing caprock should enable CO₂ storage in produced hydrocarbon shales to have the same low risks as geologic CO₂ storage in saline formations.

6 Conclusions

Increased interest in the potential storage of CO₂ in depleted hydrocarbon-bearing shales has led the US-DOE-NETL to develop a screening-level methodology for estimating the prospective storage resource of these formations. Only a small fraction of these formations will be considered for CO₂ storage because the vast majority of shale formations are expected to be impermeable sealing layers that act as caprocks for CO₂ storage. The goal is to develop a method that effectively estimates a representative range of prospective CO₂ storage resource given significant uncertainties. The resulting estimates can then be used to inform high-level decision making related to carbon storage initiatives at the national and regional scale. Three criteria were identified for prospective shale formations for CO₂ storage: 1) natural gas must have been produced from the shale by horizontal drilling and high-volume hydraulic fracturing, 2) the portion of the shale being assessed must be at depths sufficient for CO₂ to exist in a dense, typically supercritical or liquid, state: generally at least 800 m or 2,500 ft. subsurface, and 3) a suitable seal system must be present above the storage horizon to prevent unwanted upward migration of CO₂.

The US-DOE-NETL volumetric methodology accounts for storage of CO₂ in shale as a free-gas phase within fractures and matrix pores, and as an adsorbed phase on organic matter and clays. A significant limitation to estimating the prospective storage resource in shale is the lack of pertinent quantitative geologic data. Future work will focus on improving the geological and petrophysical characterization of shale to be able to determine quantitative formation- and pore-

877 scale efficiency factors and to reduce uncertainties. A better understanding of how CO₂ behaves
878 in shale will help further refine the methodology and to establish a method with associated
879 parameter values for assessing prospective CO₂ storage in these complicated formations.
880

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