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Physicochemical factors impacting CO_2 sequestration in depleted shale formations: The case of the Utica shale

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Abstract

Fractured shale formations could serve as an attractive target formation for geologic carbon sequestration once they have been depleted of hydrocarbons. The low intrinsic permeability of the shale matrix could reduce the CO_2 leakage potential, the kerogen in the shale would provide a matrix within which the CO_2 can be permanently sorbed, and the infrastructure in place at gas production sites could all be leveraged to minimize costs. Here, a modeling framework previously developed by the authors to estimate the sequestration capacity of shale formations is extended to better capture the physicochemical realities associated with injecting CO_2 into fractured shale formations. The model uses CH_4 production data to fit key parameters about the formation and applies those to a unipore diffusion model to characterize the controlling gas transport processes. A number of parameters, including the gas diffusion coefficient, the ratio of adsorbed gas to free phase gas, water saturation and gas adsorption isotherms are considered and their effect on modeling estimates is explored. The model is found to be most sensitive to the ratio of adsorbed gas to the total gas which includes both adsorbed and free phase gas. The equilibrium adsorption parameters of CH_4 and CO_2 also have significant influence largely because published estimates for these parameters vary considerably. The effect of pore collapse following production was explored in terms of its effect on characteristic diffusion length. The results indicate that increasing this characteristics length by an order of five would triple the time it takes to complete the injection of CO_2 into the formation. Similarly, an increase in water content in the formation or in the ratio of free CH_4 to sorbed CH_4 would decrease the sequestration potential of the formation. Based on this improved constitutive understanding of the modeling inputs and the estimates, the CO_2 sequestration capacity of the Utica Shale was calculated and the results were compared with those from Marcellus Shale. The differences could be understood in terms of the distinct petrophysical properties of those two shale formations. This analysis provides recommendations about experimental directions that could be very useful for improving the accuracy of sequestration capacity models.

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1. Introduction

Efforts to mitigate the impacts of climate change will require strategies for achieving deep reductions in emissions from the largest anthropogenic sources such as power plants. Geologic carbon sequestration (GCS) is an example of such a strategy and it is one that has been studied widely over the past decade [1]. GCS is the injection of CO_2 into deep formations such as saline aquifers and depleted oil and gas fields [2]. It is an attractive approach because it could be readily scaled up so that large volumes of CO_2 are being injected and because target repositories, such as saline aquifers, are available in most parts of the world [3]. Despite its promise, GCS has not been widely deployed because of the costs of capture and injection and because of concerns surrounding leakage from target repositories, the majority of which are already filled with connate brines [4].

Over the past several years, a number of groups have proposed the use of fractured shale formations that have been depleted of hydrocarbons as target repositories for GCS [5]–[8] . Depleted shale formations have a number of benefits over other repositories. Most importantly, the production of gas and oil from these formations means that a large amount of pore space has been opened and the resulting volume could be used to fill with CO_2 without creating significant over pressurization in the subsurface that could contribute to leakage. Further, the chemistry of the shale matrix is such that the kerogen in the shale preferentially sorbs CO_2 over CH_4. That means a significant fraction of the injected CO_2 would adsorb to the kerogen surface rather than being mobile in the fracture network [9].

In addition to these and other physicochemical characteristics that make injection into depleted shales attractive, there are a number of logistical considerations that would make injection into fractured shales appealing. The well infrastructure used to produce gas can be repurposed for injection. This would dramatically cut down on the cost of injecting CO_2 into the subsurface [8]. At the surface, the gas pipeline distribution network could also be used to minimize the amount of new infrastructure that would be required to move the CO_2 to the wellhead. Finally, the understanding of the subsurface environment, and the monitoring that is already in place at many of these sites, would not need to be duplicated if the same wells were used for injection.

Several studies have emerged in recent years with preliminary estimates of the sequestration capacity of shale formations [6]-[7]. Predicting the sequestration capacity of depleted shale formations can be challenging because shale fracturing is a relatively new technology and there are many unanswered questions about the fundamental processes that govern gas and liquid transport. As a result, estimates on the natural gas production side vary by several orders of magnitude [10]-[11]. Similarly, the methods used to estimate the sequestration capacity of "conventional" GCS repositories, like saline aquifers, also vary by orders of magnitude. Uncertainty related to structure and heterogeneity in the subsurface as well as to the chemical reactions and trapping mechanisms that could take place all contribute to the variability in these estimates [12].

Zhou et al. [13] and Juanes et al. [14] separately proposed methods to estimate the CO_2 storage capacity in saline aquifers. These methods are based on the available brine volume that can be replaced by CO_2. These estimates are complicated by the compressibility of CO_2 and the fact that its fluid properties are impacted by pressure and temperature profiles at depth. Perhaps the most comprehensive methodology for estimating sequestration capacity comes from the US Department of Energy, which developed a model for calculating CO2 sequestration capacity in saline aquifers, coal seams, and depleted oil and gas fields [12]. This model is based on volumetric estimates but provides considerable detail regarding the effective pore space that CO_2 can flow into. The DOE model also considers water saturation, porosity and an effective storage efficiency factor which considerably increases the data requirements of the model.

Nuttal et al. [7] estimated the capacity of the Devonian shale in Kentucky using a combination of bench-scale sorption experiments and basin scale extrapolations of formation mass. A shortcoming of this approach is that it is based on data that were obtained for ground and sorted samples and so when considering the sequestration capacity of the formation, the estimates are likely to be much higher than what could be achieved in practice. Mass transfer limitations and restrictions in terms of reactive surfaces in the fracture network are likely to limit this approach for estimating sequestration capacity.

There are few other published results about modelling the carbon dioxide sequestration in shale formation partly because of the relative lack of detailed average petrophysical parameters for these rocks. Also, the heterogeneity in a regional formation makes it challenging to scale up modelling result for a specific field or well. Our research group recently proposed a model that is based on 1) natural gas production data to estimate the gas transport parameters, 2) published sorption isotherm data and 3) large-scale production estimates to forecast the amount of CO_2 that could be sequestered in a particular site [8]. Well-scale production data is readily available for most sites that are actively being developed and the advantage of basing projections on these data is that the same factors governing CH_4 transport out of the formation are likely to impact CO_2 injection back into the same formation. A number of important parameters that will impact gas transport are captured using the gas production data including: depth of the formation, which influences pressure and temperature; matrix permeability; kerogen type and content; water content; and pore structure. The data flows that form the basis for our previous model are presented in Fig. 1.

Our model was initially applied to the Marcellus shale and it was found that over the coming decade, the Marcellus shale alone could sequester over 1 Gigatonne of CO_2 each year. This is significant given that the US as a whole produces approximately 6 Gt of CO_2 each year, of which a little over 2 Gt are from stationary sources, like power plants, which can have their CO_2 readily captured and used in carbon storage. Cars and buildings, in contrast, are more dispersed and so their ability to capture CO_2 is much lower. The Marcellus shale was selected to demonstrate the model's capabilities because it is one of the first shale plays in the United States to receive large scale production and several years of data is available with production logs for a number of unconventional wells.

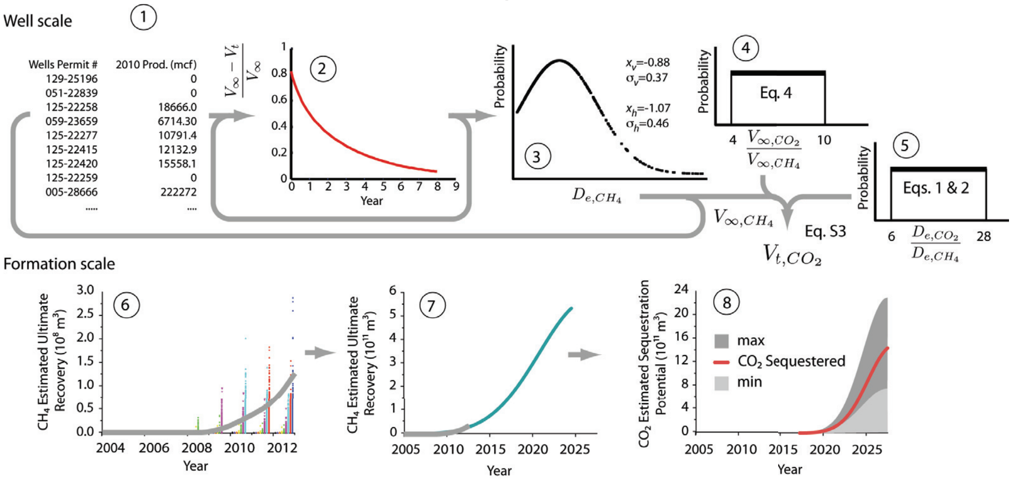

Fig. 1. Schematic of modeling framework created by the authors [adapted from [8].] (1.) Well production data for the Marcellus shale is used to (2.) calculate the ultimate yield and a gas diffusivity constant from existing wells. These data are aggregated to produce (3.) a probability density function of gas diffusivity out of drilled wells. This distribution is combined with stochastic estimates for (4.) the ratio of CH_4 volume to CO_2 volume that can sorb to the fracture surface and (5.) the ratio of the gas diffusivities at the fracture surface to estimate the volume of CO_2 that could be sequestered in these wells. At the formation scale, (6.) historical production data is used to (7.) estimate ultimate recovery for the entire formation. The well and formation-scale data are combined to get a sequestration estimate in (8.) Schematic modelling framework of our estimation for CO_2 sequestration capacity for Marcellus shale.

The goal of this work was to expand our modelling framework to include several physicochemical factors with the potential to improve the predictive capabilities of the model without considerably increasing the data input needs or the computational expense of compiling the results. In particular, the collapse of pores, especially the smallest nanopores that predominate in the kerogen matrix, following production could influence the ultimate mass of CO_2 that could be stored in a formation. Similarly, the water content of the shale could have an antagonistic impact on gas transport that may impact the production of CH_4 differently than it impacts the injection of CO_2. Finally, some of the modelling parameters that were assumed in the first version of the model were varied in magnitude to explore their effect on the modelling estimates. The enhanced model was then applied to the Utica shale in Ohio to provide complementary estimates of sequestration capacity that can help put the original Marcellus estimates into perspective. The results are presented in a way that can help develop cause-and-effect relationships related to the underlying modelling parameters and the effects on predictive capability.

2. Model

Nomenclature

D	Intrinsic gas diffusivity coefficient
D_{e,CO_2}, D_{e,CH_4}	Effective gas diffusivity coefficient of CO_2 and CH_4 through shale. *De* is derived using Eq. 5 in our previous work [8].
$D_{e,CO_2}/D_{e,CH_4}$	The ratio of effective gas diffusivities,
r_p	Characteristic distance for gas to transport
V_∞	Ultimate volume of gas
V_{∞,CO_2}, V_{∞,CH_4}	Ultimate adsorption volume of CO_2 and CH_4 on the shale fracture surface
$V_{\infty,CO_2}/V_{\infty,CH_4}$	Ratio of the ultimate volume of CO_2 to the ultimate volume of CH_4 in shale
V_t	Accumulated gas adsorption/desorption volume through the year t
A	The ratio of adsorbed gas to total gas
S_w	Water Saturation for shale formation

A detailed description of our model is available elsewhere but its key elements are presented briefly here to frame the results found in subsequent sections [8]. The model assumes that gas transport into and out of a shale matrix is controlled by the diffusion out of kerogen matrix. Several models have been proposed to describe this transport phenomena. A unipore model is used to capture the mass transport out of the kerogen matrix, which controls gas transport. This model will capture the petro-physical characteristics of the formation on average. Two assumptions are used to simplify the model, specifically that (1) the pore size are uniform and (2) the diffusion coefficient is not a function of pressure and location. Pores in the shale matrix range in size form nanometers to millimetres in diameter. Both organic and inorganic components provide the primary gas adsorption volume. The characteristic length of a pore is a key modelling parameter that had not been fully characterized previously. The model also relies on the equilibrium sorption capacity for CH_4 and CO_2, for which there is considerable literature data. The CO_2 sorption data appears to be sensitive to kerogen content and moisture in a way that is not described in the literature. The model also relies on the ratio of diffusion coefficient for CO_2 relative to CH_4. Finally, the model requires that the user make an assumption about the ratio of free gas to adsorbed gas. When a shale formation is fractured, some of the CH_4 that is trapped in the gas phase within pores is released and the rest is sorbed to kerogen surfaces. This ratio is important because the interpore CH_4 must be subtracted out from the production estimates to provide an estimate of the trapped CO_2 that will be sorbed to the kerogen.

The model, in its initial manifestation, has a number of advantages and a few shortcomings. Its primary advantage is its simplicity, which allows for the estimation of sequestration capacity with relatively little data input needs. It has two key shortcomings: the first is that some of the parameters described above were chosen as discrete values in the original model. Even though the model was stochastic and the three key parameters were varied using a monte carlo method, several other parameter were not. In this work, the previously built-in parameters, whose values were fixed are set to be statistically distributed. A comparison of the parameters included in the original model and current work are listed in Table 1.

Table 1 Parameters for the unipore model to estimate the CO_2 sequestration capacity in shale formations

Parameter	Description	Original Model [8]	This work
$\frac{V_{\infty,CO_2}}{V_{\infty,CH_4}}$	Adsorption capacity derived from isothermal adsorption for CO_2 and CH_4	Uniformally distributed 4-10	Uniformally distributed 4-10
$\frac{D_{e,CO_2}}{D_{e,CH_4}}$	Diffusion coefficeint for CO_2 and CH_4 in shale	Uniformally distributed 6-28	Uniformally distributed 6-28
r_p	Gas transport distance before arrive at large fracture surface	Fixed at 0.002m	Discrete value of 0.002m,0.01m, 0.02m, 0.05m
A	The ratio of adsorbed gas to total gas	Fixed at 0.5	Uniformally distributed 0.33-0.67
S_w	Water Saturation for shale formation	Not included	Uniformally distributed 0.1-0.3

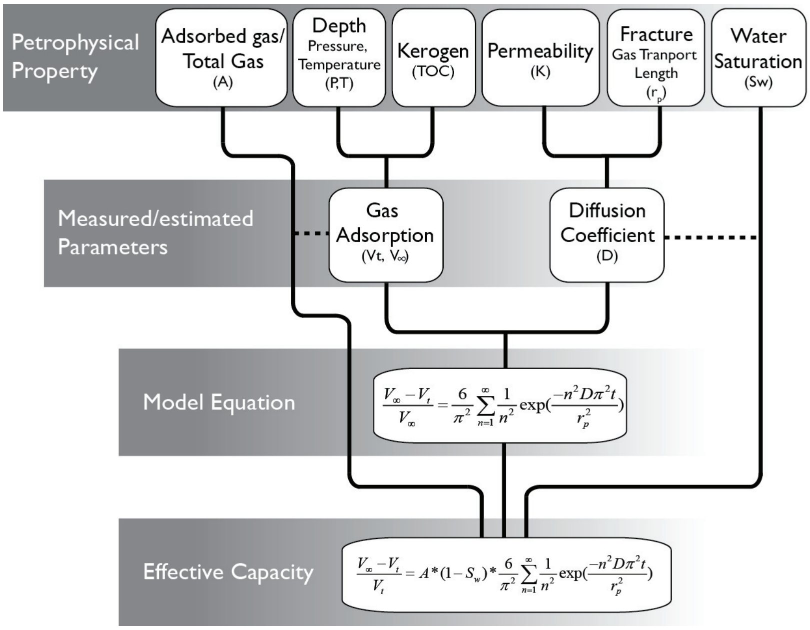

Fig. 2. The schematic illustration of the relationship between physicochemical parameters and the model used to estimate CO_2 sequestration capacity of shale formations. The solid line indicates a direct relationship. The dashed line indicates that the relevant petrophysical property could have influence to the measured parameters, but we don't include the influence in our model.

Table 1 lists the modeling parameters but does not offer much insight into the connections between parameters or the underlying physicochemical processes that they describe. Consequently, Fig. 2 is provided to show the relationships between physicochemical properties, parameters that are abstracted from these fundamental properties, the model and how all these factors are combined to provide a quantitative estimate of sequestration capacity. In particular Fig. 2 reveals how certain parameters, e.g., the water saturation of the shale and the ratio of absorbed to total gas in the formation, do not influence the estimates of total sequestration capacity based on the pore model but are used as scaling factors on the final estimate.

3. Results and Discussion

The effect of the model parameters described in Table 1 and Fig. 2 were each explored in detail and the results are presented in the following sections. In general, the ratio of adsorbed gas to gas in place (GIP, including both adsorbed gas and free phase gas) and the equilibrium adsorption ratio have the biggest impact on the model output. Fig. 3 presents a sensitivity analysis in which the mean value for each parameter was varied by 10%, without any change to the structure of the distribution, and the results show that corresponding change in the model estimate. A and $\frac{V_{\infty,CO_2}}{V_{\infty,CH_4}}$ both elicit a change of approximately 10% in the model estimate while the other model inputs have a more muted impact on the estimates. Water saturation (S_W) and the ratio of CH_4 diffusivity to CO_2 diffusivity ($\frac{D_{e,CO_2}}{D_{e,CH_4}}$) have less impact. The effect of CH_4 diffusivity (D_e) is the least pronounced.

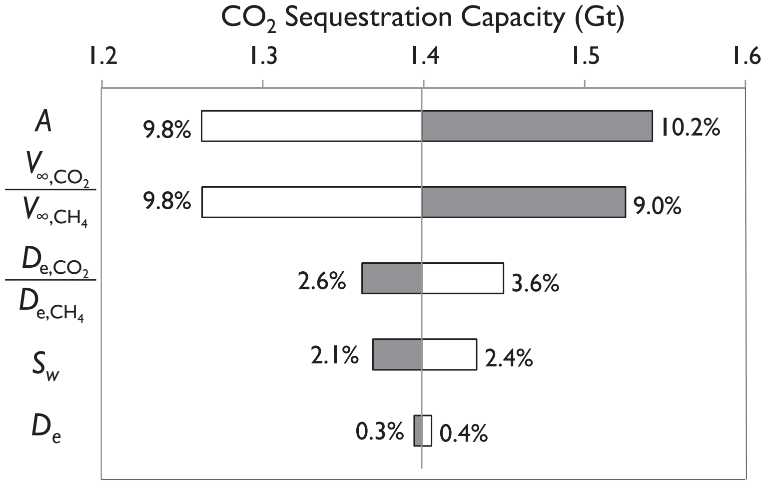

Fig. 3. Sensitivity analysis of different parameters to the total CO_2 sequestration capacity. Gray bars are the capacity when the parameter is increased by 10%. White bars are the capacity when the parameter is decreased by 10%. The percentage changes of the sequestration capacity under different scenarios are also shown in this figure.

These sensitivities in the model are consistent with the computational structure of the model presented in Fig. 2. The ratio of adsorbed and free gas is incorporated into the results as a final step and so it follows that the results are almost directly proportional to changes in the input. The model estimates are also directly correlated with the equilibrium sorption ratio because appears in the equation outside of the exponent. In contrast, the ratio of the diffusivity of CO_2 and CH_4 are negatively correlated with model output (oberseved by the shading in the bars in Fig. 3). Water saturation also has a negative correlation with the model output because higher water content impacts the availability of pore space and binding sites for CH_4 sorption.

3.1. Adsorption capacity (V_t, V_∞)

The gas adsorption capacity, which is the equilibrium mass or volume of CO_2 that can exist on the kerogen surface, is known to be impacted by both the geological and petrophysical properties of the shale formations, such as depth, organic content, water saturation, porosity, etc. [9]. The pressure and temperature of a particular formation is a function of the depth of the formation and its location (i.e., geothermal gradients vary geospatially). At higher pressures, more of the fluid can occupy the available site on the surface of the shale. However, the fluid molecules will desorb when the pressure decreases, which is always happening during oil/gas extraction [15]. Similarly, less fluid will sorb at higher temperature because of the higher energy in the system. This behaviour is well understood and can be characterized for this application using classical Langmuir isotherms for either CH_4 or CO_2 on shale samples [7]. Total organic content (TOC) is the other important factor for evaluating the gas adsorption potential. Most of the TOC in shales is kerogen, a high molecular weight organic compounds that predominates in sedimentary rocks and it contains most of the methane and hydrocarbon liquids trapped in its matrix. Kerogen makes up anywhere between 2-10% by mass of the shale in the Utica or Marcellus formations. Yang et al. [16] demonstrated the positive relationship between TOC and gas capacity. Others have characterised the micro/macro pores in kerogen using SEM [17] and mercury injection [16] to illustrate the role of kerogen content and structure on controlling gas and liquid transport out of the bulk shale rock. Although clay minerals have also been shown to adsorb fluid and provide pore networks [18], kerogen is still considered as the main source to store gas.

In our original paper, the sorption capacity values from a variety of papers were compiled to produce a constitutive relationship between TOC content and the equilibrium sorption capacity (as shown in Fig. 4 reproduced from [8]. It is interesting to note in this figure that the scatter in the CO_2 data is considerably higher than the scatter for the CH_4 data. This could have to do with the fact that CO_2 is much more sensitive to moisture content in the kerogen, the age of the rock (and by extension the chemistry and structure of the kerogen) and the temperature and pressure. The general trend gleaned from these data is that CO_2 sorbes preferentially to kerogen relative to CH_4 but the extent to which it is preferred requires additional experimental work to fully characterize the influence of shale physicochemical factors on driving the predictions of modelling efforts.

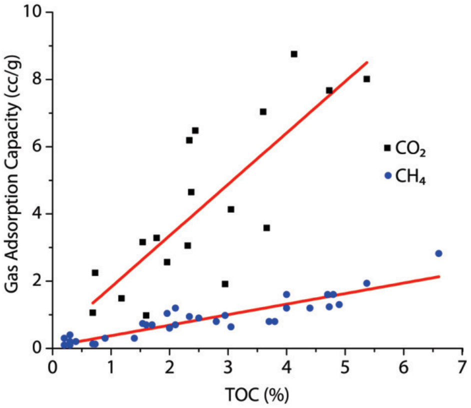

Fig. 4. Sorption characteristics of CH_4 and CO_2 on ground shale samples (adapted from [8]). Note the scatter in the CO_2 data suggesting that CO_2 sorption is more sensitive to factors like moisture and kerogen composition, aspects that have not yet been characterized in the literature.

3.2. Characteristic gas transport distance (r_P)

Modeling the kinetics of CH_4 production and CO_2 injection into a kerogen matrix using the unipore model requires some assumptions about the characteristic distance that the CH_4/CO_2 needs to diffuse through the pore. We initially modeled this parameter (r_P) using a fixed value of 0.002m. The assumption here is that once the gas leaves the pore and enters the fractures that the transport is rapid. Picking a fixed value for r_P could ignore some of the complexity that exists in shales in terms of kerogen deposit heterogeneity. It also ignores the possibility that pores can collapse because of the increased effective stress induced by the decrease of pore pressure after CH_4 extraction. This could increase the transport distance for CO_2 molecules, relative to the r_P that was assumed based on the CH_4 extraction data. To explore the role of r_P on injection kinetics, its effect on completion ratio were calculated. Completion ratio is defined as the time it takes from the start of CO_2 injection until the well is saturated with CO_2. Four values (1X, 5X, 10X and 25X of the original value) for r_P were selected based on literature analysis of kerogen pore structure. Pore collapse was not explicitly considered here but it could be assumed to have a net effect of raising the effective pore length of a formation. The increase in r_P from 0.002 to 0.02 m has a dramatic impact on how long it would take to fill the well with CO_2. At the highest lengths of r_P, the well would not be completed in the 20 years that we modeled. Developing a better phenomenological relationship among kerogen age/structure, pore pressure change after gas extarction and r_P would aid greatly in developing accurate forecasts that will directly drive the economics of CO_2 injection into depleted shales.

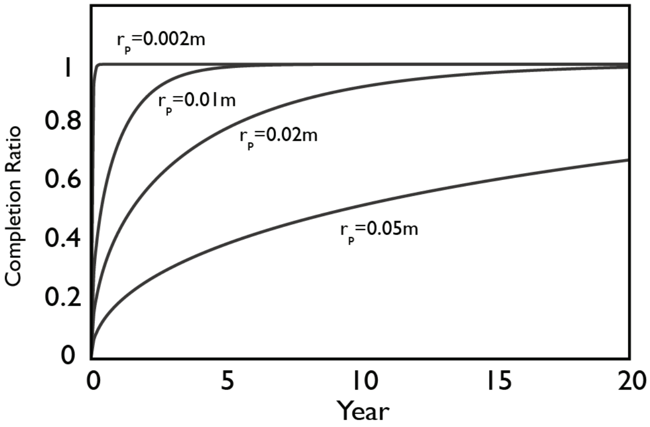

Fig. 5. The characteristic gas transport distance (r_p), which is a key parameter in the unipore model, has an important effect on the kinetics of gas transport through the shale formation and can greatly increase the time it would take to refill a formation with CO_2. Here the completion ratio for a well is plotted as a function of time for a variety of representative r_P values.

3.3 Water saturation and free gas ratio

Two parameters, water saturation in the shale and the ratio of sorbed gas to GIP, will have important impacts on the predictive capabilities of shale sequestration models but do not factor into the interpore model. Water saturation has important impacts on multiphase flow and wettability characteristics in the formation, which can interfere with gas transport through meso- and nano-scale pores. This water would also compete with CO_2 for free pore space and the time between CH_4 production and CO_2 injection (which would typically be on the order of years) would be enough for many of the pores to fill with connate brines from surrounding formations. Free gas ratio is important because, as described earlier, many of the pores that are being accessed in the fracturing process are not being resealed during the reinjection process. We model only the CO_2 that is sorbed in the kerogen matrix and assume that the CO_2 in the fractures and pores may be mobile and/or replaced by CO_2 saturated brines. Both the Marcellus and the Utica formations are considered to be relatively dry shales and so the water saturation was set to a uniform distribution between 10% and 30% [19]–[21]. The Adsorbed/Free gas ratio is set between 1/2 and 2/1 for both shales. The results on the sequestration potential in the Utica shale are presented in Fig. 6.

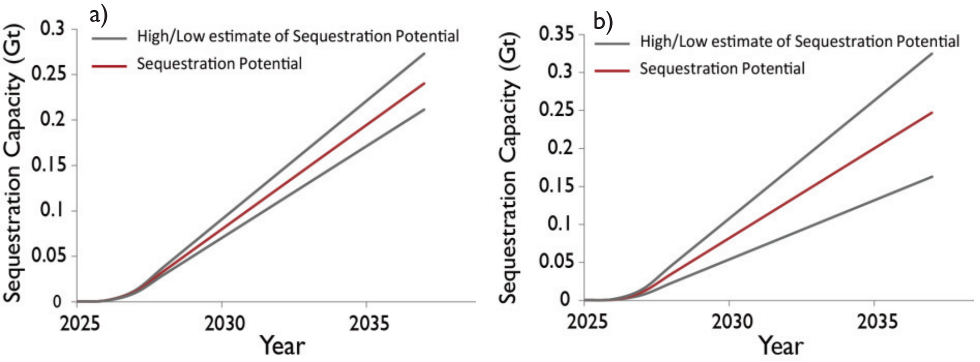

Fig. 6. a) Water saturation (S_w) and b) adsorbed/gas in place are both important parameters that are not captured using the unipore model but are included as a post-processing step to produce estimates that are sensitive to these effects. Here high estimates are water content = 10%, free gas ratio = 33% and low estimates are water content = 30%, free gas ratio = 67%.

3.4. Overall estimate for Utica Shale

This analysis of the different parameters impacting our estimates of shale sequestration capacity were combined and applied to the Utica Shale in Ohio. The Utica Shale has been developed more recently than the Marcellus Shale and so less data is available. It is also smaller than the Marcellus shale in terms of recoverable resources. The Utica shale is projected to contain 2.1×10^{11} m^3 of CH_4 while the Marcellus is thought to contain 4.9×10^{11} m^3 based on linear projections from the US Department of Energy [8]. The two formations do share some common petrophysical characteristics. For example, the water saturation profiles of the two formations are similar even though the exact water content can vary regionally. Also, the ratio of adsorbed gas to free phase gas are not thought to vary between the formations. However, there are some important differences. The kerogen types of the Marcellus and Utica shales are different because of their age and this could lead to different gas adsorption and transport properties. Also, the Marcellus shale produces mostly "dry gas" in which CH_4 is the primary hydrocarbon component. The Utica shale produces more natural gas liquids, particularly towards the western part of the formation. The diffusivity of CH_4 in the Utica shale ($4.23 * 10^{-10}$ m^2/day) that we derived from production data is 3-4 times higher than the estimate for the Marcellus shale ($1.34 * 10^{-9}$ m^2/day). This could be attributed to the different petrophysical properties of those two shales. It is also worth noting that Utica shale is more than 3000 feet deeper than the Marcellus shale, which results in a pressure differential of nearly 7 MPa. The higher stress and pressure within the Utica shale could lead to higher gas flow properties, such as larger absorbed gas amount and higher production rate. But it could also contribute to pore collapse following hydrocarbon extraction. Taking these factors together, the model indicates that the Utica shale has a much lower sequestration capacity than the Marcellus shale (1.4 Gt vs. 12 Gt) based on current projections of recoverable resources in both formations. It is worth noting that the Utica shale has approximately 80-90% fewer wells than the Marcellus shale and so developing robust parameters from this limited data is a challenge. As estimates are improved, more well data is published, and some key petrophysical characteristics are explored in the lab, these estimates could be further refined. In the meantime, the very large sequestration potential of these formations suggests that additional research into using depleted shales for CO_2 sequestration merits further consideration.

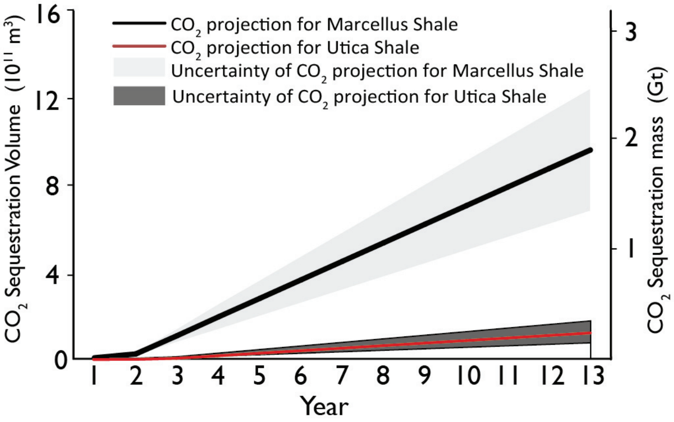

Fig. 7. Comparison of CO_2 sequestration capacity for the Marcellus and Utica Shale. The estimates for the Marcellus shale are considerably higher but so are the total recoverable resources from that formation.

Acknowledgements

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