Simulation of Adsorption Mechanisms of Methane and Carbon Dioxide in Shale Matrix

J. I. Guillamon[1], A. López Manriquez[1].
1. Department of Chemical & Natural Gas Engineering, Texas A&M University-Kingsville, Kingsville, Texas, USA.

Abstract: The aim of this study is to model CH_4 and CO_2 adsorption in shale reservoirs at micro to nano-scale by the use of COMSOL Multiphysics. The modeling of both physics, gas flux and adsorption, have been accomplished applying the Transport of Diluted Species in Porous Media module. Adsorption of CH_4 and CO_2 in shale matrix, assuming no water content, was analyzed by using Langmuir, Freundlich, and Brunauer-Emmett-Tellet (BET) Isotherm models. Freundlich and BET adsorption models are not restricted to monolayer formation and could be considered as a potential approach for modeling under water presence. These adsorption models were coupled with an equation for gas flux from the fracture to the shale particle surface. As a first approximation, the Wilke model was used to compute gas flux due to its simplicity and minimum computational requirements. Because former studies state that Knudsen diffusion should be considered for a more accurate representation of gas flux through the nano-porous matrix, Wilke-Bosanquet equation was also implemented as a second approximation for the flux modeling. Our results indicate that Langmuir and Freundlich adsorption models provide similar values. A small deviation was found at low pressures. Therefore, it was concluded that Freundlich model can be used for modeling gas adsorption in shales under conditions where the existence of monolayer is not guaranteed.

1. Introduction

Climate change is an alteration in the weather pattern caused by the increment of greenhouse gases molecules in the atmosphere. Carbon dioxide has been identified as the gas with major contribution to the greenhouse effect (EPA 2016). The United Nations Intergovernmental Panel for Climate Change (IPCC) has proposed several measures for climate change mitigation. Carbon capture and storage (CCS) is considered one of the mechanisms with greater impact for mitigation of global warming (EPA 2016). The main types of formations to be considered as a potential long-term storage of carbon dioxide are: depleted oil and gas reservoirs, saline formations, coal beds, basalts and unconventional oil and gas reservoirs (shale).

Although carbon sequestration is considered a necessary measure to apply in order to substantially decrease carbon dioxide emissions, the high costs of this technique has deferred its development. The synergy of CCS with other commercial activities, like oil and gas production, is essential for CCS deployment. Carbon dioxide sequestration in gas reservoirs has the potential of enhancing natural gas production while storing the CO_2 on a secure storage site. Besides, the possible increase in methane production with its prominent increase in revenues could be an economic trigger to motivate the carbon capture and sequestration.

Shale gas reservoirs have shown some benefits compared with other gas formations for the purpose of carbon sequestration. The organic matter of shale formations (kerogen) could act like a molecular sieve giving preference to CO_2 adsorption (Kang *et al.* 2011). Hence, shale formations have an outstanding potential for carbon dioxide sequestration.

According to Kang *et al.* experimental results, shale gas reservoirs hold a large amount of gas which is produced through desorption mechanisms. Gas desorption phase starts once the free gas present in the formation fractures has already been produced and the reservoir starts depleting. Once formation pressure starts declining, gas desorbs from shale nano-pore surface and turn to free gas in the reservoir fractures. This desorption mechanism is usually represented by the Langmuir isotherm equation and the gas flux through the shale matrix is often defined by diffusion mechanisms instead of convection forces (Mengal and Wattenbarger 2011).

In addition to CH_4 adsorption/desorption mechanisms, there is high interest in studying CO_2 adsorption to estimate the potential for Enhance Oil Recovery (EOR) as well as carbon sequestration. According to Kang *et al.* (2011), CO_2 shows higher adsorption capacity than CH_4. Their laboratory results successfully fit Langmuir isotherm model.

In order to have a better understanding of how individual mineral constituents of shale reservoirs contribute to the gas adsorption, Heller and Zoback (2014) performed laboratory tests to measure CH_4 and CO_2 adsorption in four different shale samples (Barnett, Eagle Ford, Marcellus and Montney shale reservoirs), as well as in three other pure mineral samples, pure carbon, illite and kaolinite. The authors showed that all their laboratory results successfully fit Langmuir isotherm model and are congruent with Kang *et al.* findings. CO_2 has a higher adsorption capacity than CH_4. Under their experimental conditions, CO_2 molecules had been

adsorbed two to three times more than CH_4 molecules. These findings have been corroborated in both pure mineral samples and shale samples. The authors highlight that the experiments have been performed under drained conditions (dray samples), recognizing that results might be different under water presence. If water is present in the core sample, gas molecules will have to compete with water molecules for adsorption sites availability. However, clay minerals are highly hygroscopic, contributing to a higher preference for water molecules adsorption (Heller and Zoback 2014).

Sun et al. (2013) and Prajapati and Mills (2014) modeled the flux of gas in shale matrix and coupled it with the Langmuir adsorption mechanism using COMSOL Multiphysics. Sun et al. manifested that Darcy´s law does not represent properly gas transportation in shale reservoirs due to their ultra-fine pore sizes. They described gas transport phenomena in a double porosity system using the Dusty Gas Model (DGM) incorporating mechanisms of viscous flow as wells as Knudsen diffusion and ordinary diffusion processes. In this study, the gas transport mechanisms in porous media have been coupled with an adsorption process represented by the Langmuir adsorption isotherm.

Prajapati and Mills investigated CH_4 and CO_2 flux in shale matrix by modeling the flow equations combined with the Langmuir adsorption isotherm. The authors assert that gas flow mechanisms in shale reservoirs can be described by the steps of slip flow, diffusion and sorption at micro-pore level, and by Darcy's law at fracture level. The authors analyzed the CH_4-CO_2 mixture flux in shale matrix considering four different flow models: Wilke, Wilke-Bosanquet, Maxwell-Stefan and DGM. They inferred that the DGM contains the key terms to accurately model the gas flow through the porous matrix (Prajapati 2014).

Jin and Firoozabadi (2014) performed numerical simulation to explain the dynamics at molecular level during CH_4 and CO_2 adsorption in clay. They identified that, under water presence in porous media, water competes with CO_2 or CH_4 for surface area in small nano-pores, and in other cases CO_2 or CH_4 form a weak second adsorption layer. This phenomenon cannot be modeled by a Langmuir adsorption isotherm. Feng et al. (2018) have measured the N_2 adsorption capacity of clay samples under different water content and fit their results under a multilayer adsorption model. They inferred that the adsorption contribution to gas storage might be diminished under high water presence.

Several studies have been done related to CH_4 and CO_2 adsorption in shale reservoirs. However, not much attention has been focus on analyzing if the Langmuir model is the most appropriate option for modeling the gas adsorption process.

Considering that a better understanding of CO_2 adsorption mechanisms in rock matrix might represent a great aid for Carbon Capture and Storage techniques development, the aim of this study is to compare different adsorption models and to inquire into how the different adsorption models can affect the gas adsorption in shale reservoirs. Adsorption of CH_4 and CO_2 in shale matrix will be analyzed by using Langmuir, Freundlich, and Brunauer-Emmett-Tellet (BET) Isotherm models. These adsorption models will be coupled with an equation describing the gas flux from the fracture to the shale particle surface. Gas flux and adsorption mechanisms will be modeled using COMSOL Multiphysics.

2. Model Definition

The dual-porosity approach is one of the most frequent methods to study gas transport on a shale reservoir, which mainly consists of a shale matrix connected by a fracture network (Fathi and Akkutlu 2012). The shale matrix is composed of inorganic material (mostly illites and smectites) and organic matter (kerogen). The dual-porosity approach consists of a matrix that is defined by low porosity and ultra-low permeability and a fracture systems with relative low porosity and high permeability (Akkutlu and Fathi 2012). Most of the gas will be adsorbed in the organic-rich material. According to Akkutlu and Fathi, the fracture system is supposed to be communicated hydraulically with the inorganic section and the latter is in continuity with the organic-matter pore network.

Model Assumptions:

Numerical simulation is performed considering the following assumptions: (1) single-phase gas flow; (2) all species follow the ideal gas law; (3) constant reservoir temperature; (4) rock compressibility remains constant; (5) isotropic behavior of rock matrix; (6) porosity of fracture and matrix media remains constant; (7) infinity boundary reservoir effects; (8) gravity effects not taken into consideration.

Governing Equations:

The mass balance equation for a binary mixture in a shale matrix could be expressed as:

$$\frac{d\left(\rho.\phi_m + \rho_q.(1-\phi_m)\right)_i}{dt} + \nabla.(\rho u)_{m,i} = 0 \quad \cdots\cdots\cdots\cdots (1)$$

where $i=1$ (CH_4) and $i=2$ (CO_2), ρ is gas density at reservoir conditions, Φ_m is matrix porosity, ρ_q is the gas density of the adsorbed gas and $(\rho u)_{m,i}$ is the mass flow of component i in the matrix. Sun et al. defined the gas density of adsorbed gas as:

$$\rho_{q,i} = \frac{\rho_s.M_i}{V_{std}} \times q_{ads,i} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

where ρ_s is the rock density, M_i is the molar mass of component i, V_{std} is the standard molar volume and

$q_{ads,i}$ is the amount of gas adsorbed in the rock surface.

The last parameter is obtained from the adsorption equations. The mass balance will consider sorption and diffusion as the main mechanisms for gas flow in the matrix. In this study, comparison between different adsorption models will be performed.

Adsorption Mechanism:

Several models have been developed to describe the process of adsorption of gas molecules on a solid surface. The following are some of the most used adsorption isotherm models, which this study considers to have the better approach to model the gas flux in shale matrix system.

Langmuir Isotherm model:

Empirical model, widely applied due to its simplicity and robustness. It assumes that adsorption can occur in one molecule in thickness layer at a fixed number of sites, which are identical and equivalent (homogenous adsorption). If more than one component is considered, the model can be represented as:

$$q_{ads,i} = \frac{V_{L,i}.B_i.P_i}{1+\sum_{j=1}^{n} B_j.P_j} \quad \dots\dots\dots\dots\dots\dots\dots\dots \text{(3)}$$

Freundlich Isotherm model:

Describes non-ideal relationship and reversible adsorption, not restricted to monolayer formation. It is widely used for modeling heterogeneous systems particularly for organic compounds. According to Foo and Hameed (2010), Freundlich isotherm does not follow Henry´s law at low concentrations. Equation 4 expresses Freundlich Isotherm.

$$q_{ads,i} = K_F.P_i^{1/n} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(4)}$$

Brunauer-Emmett-Teller (BET) Isotherm model:

Theoretical equation widely used to model gas-solid equilibrium systems consistent with multilayer adsorption, which can be expressed as:

$$q_{ads,i} = \frac{q_s.P_{BET}.P_i}{(P_s - P_i)\left[1+(P_{BET}-1)(P_i/P_s)\right]} \quad \dots\dots\dots\dots \text{(5)}$$

Considering that the gas behaves as an ideal gas, the above equations can be expressed in terms of concentration.

Gas Transport Mechanism:

Several models have been developed to evaluate gas diffusion in porous media. When considering multicomponent species transport, Wilke model is the most robust derivation of the

Fick´s law (Solsvik and Jakobsen 2012). Wilke-Bosanquet model couples molecular diffusion with the Knudsen diffusion. This approach could be of great interest for this study due to the presence of nano-pores in the shale matrix.

Wilke model:

$$N_i = \left(-D_{ei,m}.\nabla C_i\right); D_{ei,m} = \frac{1}{\sum_{j=1;\, j\neq i}^{n}\left(x_j/D_{ij}^e\right)} \quad \dots\dots\dots\dots \text{(6)}$$

Wilke-Bosanquet model:

$$N_i = \left(-D_{i,eff}.\nabla C_i\right); \frac{1}{D_{i,eff}} = \frac{1}{D_{ei,m}} + \frac{1}{D_{k_i}^e} \quad \dots\dots\dots\dots\dots \text{(7)}$$

where $D_{ki}{}^e$ is the Knudsen diffusion for specie i and $D_{i,eff}$ is the effective diffusivity of gas specie i. Knudsen diffusion could be computed as:

$$D_{ki}^e = \frac{\phi_m}{\tau}.\frac{d_{pore}}{3}.\sqrt{\frac{8.R.T}{\pi.M_i}} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(8)}$$

where R is ideal gas constant, T is the temperature of the reservoir, M_i is the molecular weight of gas specie i, d_{pore} is the pore diameter and τ is the tortuosity.

3. Use of COMSOL Multiphysics

The previous system of non-linear equations that describe gas flux through the shale porous matrix are solved using finite element software, COMSOL Multiphysics 5.3a. The transport of diluted species in porous media module was used to simulate the effect of the various physics in the model domain. Pardiso solver was selected to solve the differential equations. The tolerance factor was set to 0.1 and the software was set to do not perform more than 5 iterative steps. Regarding the meshing of the system, several mesh element size have been tried without changes in the final simulation results. Therefore, a physics-controlled mesh has been selected for the modeling of the system, with the finer element size.

Figure 1 shows a schematic for representing the gas injection in the shale matrix system.
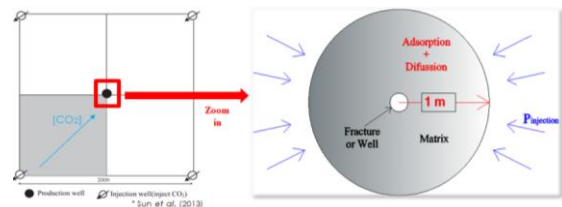
Figure 1. System Description. To the left, top view of a field with a production well and four CO_2 injection wells at the corners. To the right, a zoom view of the production well surroundings, which will be used as the domain for our study.

The initial condition imposed to the system is:

$$P_{m,i}(x, y, t)\big|_{t=0} = P_{initial} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

where $P_{initial}$ is the reservoir initial pressure.

Boundary conditions are set to be:

$$(\rho u)_{m,i}\big|_{\Gamma_1} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

$$\nabla(\rho u)_{m,i}\big|_{\Gamma_2} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

where Γ_1 represents the outer boundary of the shale matrix and Γ_2 represents the boundary between the shale matrix and the fracture.

4. Results and Discussion

Table 1 presents the basic parameters used for the simulation (Sun *et al.* 2013).

Table 1. Reservoir and gas parameters.

Porosity	8%
Permeability (m^2)	1.0E-19
Rock density (kg/m^3)	2560
Rock compressibility (1/Pa)	1.0E-05
Tortuosity	4
Reservoir Temperature (K)	353
Pore diameter (nm)	20
Molecular Diffusion (cm^2/s)	1.0E-08
Initial Pressure (Pa)	2.5E+06
Injection Pressure (Pa)	1.0E+07

Table 2 shows the different adsorption models parameters needed for the study. Data used in this study have been obtained from Heller and Zoback (2014). They researched using Eagle Ford Shale samples. They measured adsorption capacity of several shale and clay samples and fit their results to the Langmuir adsorption model. Freundlich and BET isotherm parameters have been obtained by lineal regression fitting of data constructed using the Langmuir adsorption parameters obtained by Heller and Zoback.

Table 2. Adsorption mechanisms parameters.

|	
Langmuir volume of CH$_4$ (*std.ft^3/kg*)	1.27E-02
Langmuir volume of CO$_2$ (*std.ft^3/kg*)	3.31E-02
Langmuir pressure of CH$_4$ (*psi*)	694.7
Langmuir pressure of CO$_2$ (*psi*)	409.6
Freundlich ads. const. for CH$_4$ (*mol/kg*)	1.10E-04
Freundlich ads. const. for CO$_2$ (*mol/kg*)	6.14E-05
Freundlich ads. exp. for CH$_4$	2.114
Freundlich ads. exp. for CO$_2$	1.503
BET sat. capacity for CH$_4$ (*mol/kg*)	5.43E-03
BET sat. capacity for CO$_2$ (*mol/kg*)	1.15E-02
BET ads. pressure of CH$_4$	26.7
BET ads. pressure of CO$_2$	43.8
Saturation pressure of CH$_4$ (*psi*)	2500
Saturation pressure of CO$_2$ (*psi*)	1100

In order to contrast the difference in flux and sorption mechanisms between the two different gases, the model assumes that at the injection boundary, CH$_4$ and CO$_2$ are introduced in a 1:1 molar ratio.

This work compares the results obtained using three different adsorption models and two gas flux models. The discussion will start by the comparison of the two gas flux models: Wilke vs. Wilke-Bosanquet.

Figure 2 and Figure 3 show the concentration change for two different flux models evaluated at the matrix-fracture interface (Γ_2). In both plots the adsorption model is described by the Langmuir Isotherm. In the first graph, gas flow is represented by Wilke flux model, while in the second one Langmuir model is coupled with Wilke-Bosanquet equation. From these plots, it could be expressed that CH$_4$ profile reaches faster the injection concentration at the outer boundary domain than the CO$_2$ profile. This is in agreement with the fact that if carbon dioxide presents higher adsorption capacity, more CO$_2$ will be adsorbed in the porous matrix and hence, less CO$_2$ will continue flowing through the domain comparing to CH$_4$.
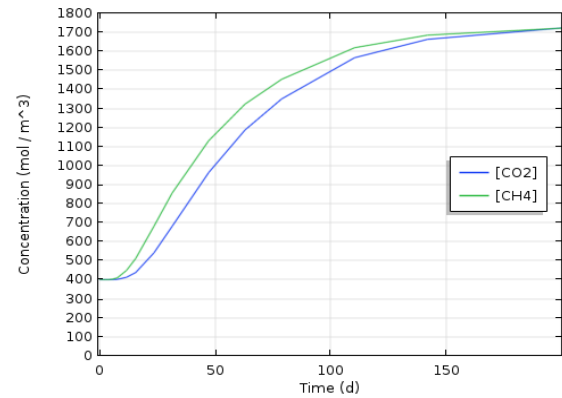
Figure 2. Concentration history plot for Langmuir adsorption isotherm coupled with the Wilke flux model.
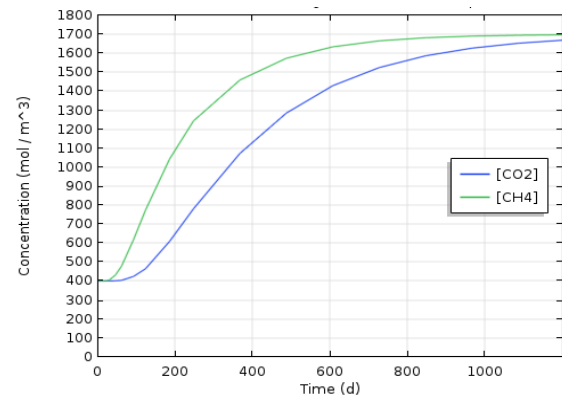

Figure 3. Concentration history plot for Langmuir adsorption isotherm coupled with the Wilke-Bosanquet flux model.

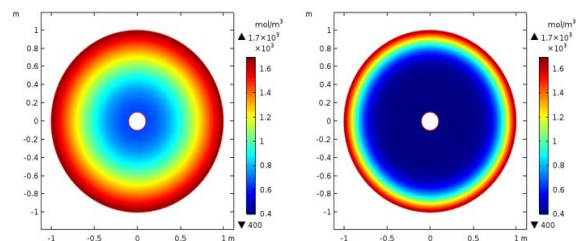By comparing Figure 2 and Figure 3, it could be inferred that implementing Wilke-Bosanquet model

takes more time to reach injection concentration than the Wilke prototype. As a result, Wilke-Bosanquet flux model indicates that more time is needed for the gas species to get adsorbed in the porous media. Statement that is in agreement with the findings of Prajapati and Mills (2014).

Figure 4 illustrates contour plots of gas concentration profiles at 30 days of injection. The simulation is done implementing the Langmuir adsorption isotherm and the Wilke flux model. These contour plots support the previous observation that CH_4 molecules flow faster CO_2 through the shale domain.
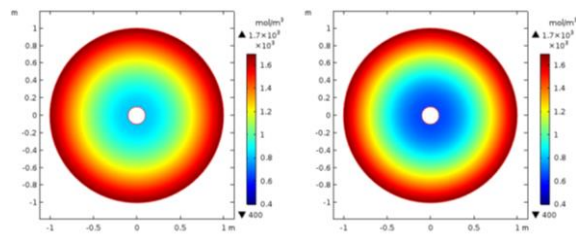
Figure 4. Gas concentration profile at 30 days of injection. To the left, CH_4 concentration profile. To the right, CO_2 concentration profile.

Figure 5 compares contour plots of gas concentration profiles using Langmuir adsorption model and at 30 days of injection, including the Wilke and Wilke-Bosanquet flux models.


Figure 5. Concentration profile for CO_2 with Wilke flux model (left) and Wilke-Bosanquet (right) at 30 days of injection.

As it was shown when comparing Figure 2 and Figure 3, analysis of Figure 5 confirms that Wilke-Bosanquet model takes more time to reach the injection concentration than the Wilke flux model. This difference could be inferred to be because of the effect of the Knudsen diffusion slowing down gas flux through the porous media.

Subsequently, the study is going to show the comparison between the different adsorption mechanisms proposed: Langmuir, Freundlich, and BET. In order to contrast the different models, these adsorption models will be coupled with the Wilke-Bosanquet gas flux equation.

Figure 6 illustrates gas concentration history plot evaluated at the outlet boundary, for the model composed of the Wilke-Bosanquet flux equation coupled with the Freundlich adsorption isotherm. As it happened with the Langmuir adsorption model,

the curve presents a sigmoidal shape. This means that adsorption occurs up to a concentration value where the medium began to get saturated. Besides, this plot also shows that CH_4 flows faster through the porous media than CO_2.
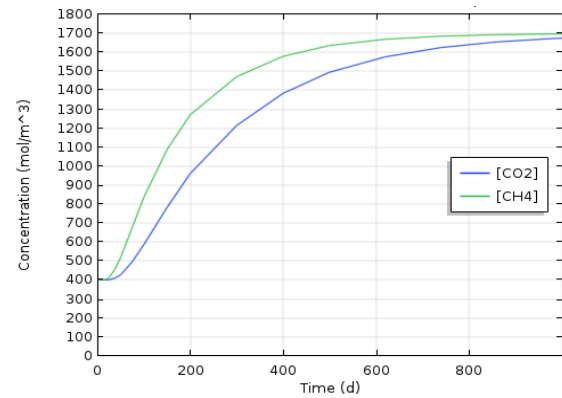
Figure 6. Concentration history plot for Freundlich adsorption isotherm coupled with the Wilke-Bosanquet flux model.

Figure 3 and Figure 6 represent the effect of implementing Langmuir and Freundlich adsorption models coupled with the Wilke-Bosanquet flux model, respectively. From this comparison it could be expressed that when implementing Freundlich isotherm, injection concentration is obtained slightly faster than using the Langmuir adsorption model. Therefore, it could be said that under the conditions imposed in this simulation, both models give similar results. It should be highlighted that the Freundlich adsorption isotherm is not restricted to monolayer formation, a fact that could be of relevance for future studies including small presence of water (Jin and Firoozabadi 2014).

Figure 7 presents CO_2 concentration profiles after 90 days of injection, considering the Wilke-Bosanquet flux model coupled with either the Langmuir or the Freundlich adsorption isotherm.
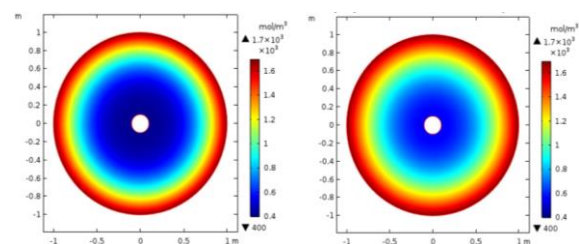

Figure 7. CO_2 concentration profile at 90 days of injection, applying the Wilke-Bosanquet´s flux model, considering the Langmuir adsorption model (left) and the Freundlich adsorption model (right).

From Figure 7 it could be asserted that after 90 days of injection, gas flows slightly faster through the porous domain under the physics defined by the Freundlich adsorption than to the Langmuir adsorption model. However, from comparing Figure 3 and Figure 6, it could be stated that both adsorption

models give similar results after 800 days of beginning gas injection. This infers that both models yield slight deviation results at low concentrations while at high concentrations both models provides similar results. It is important to stand out that the Freundlich model does not converge to Henry's law at low concentrations, which could be the cause of this slight deviation at low gas concentrations.

Figure 8 shows gas concentration history plot evaluated at the outlet boundary for the Wilke-Bosanquet flux equation coupled with the BET adsorption isotherm. The BET isotherm presents a sigmoidal shape too and also shows that CH_4 flows faster through the porous media than CO_2, as noted with the Langmuir and Freundlich adsorption model previously. However, the sigmoidal curve is not so easy to recognize as in the other models, mainly due to the fact that the BET adsorption takes a much longer time to reach the injection concentration.
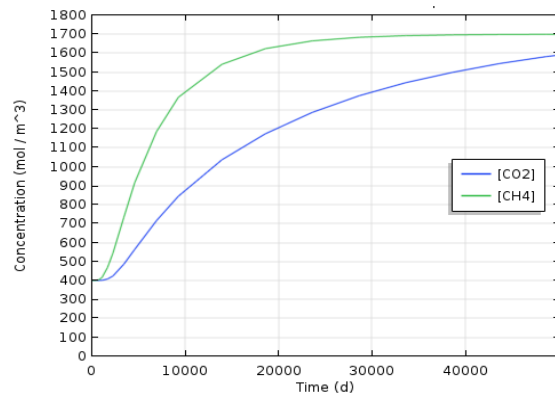
Figure 8. Concentration history plot for BET adsorption isotherm coupled with the Wilke-Bosanquet flux model.

Contrasting Figure 3 and Figure 8, it could be expressed that BET isotherm takes about 50 times the days needed by the Langmuir isotherm to reach the injection concentration.

Analyzing the continuity equation, it could be inferred that if the flux through the porous matrix is so small, there should be a term with a big consumption. This means that the BET adsorption model estimates about 50 times higher adsorption than the scenario with the Langmuir adsorption model.

Although these are preliminary conclusions from the results obtained, it should be underlined that the BET isotherm adsorption model is based on the assumption that the gas molecules form more than one layer of molecules over the solid surface (multilayer adsorption). Some authors have suggest the possibility of multilayer adsorption (Jin and Firoozabadi 2014). However, these authors stated that the multilayer formation is possible under high pressure conditions. For the purpose of this simulation, the injection pressure was assumed to be in the order of 10 MPa. Simulations at higher pressure values should be performed.

Moreover, it is emphasized that Freundlich and BET adsorption model parameters were obtained by the application of linear regression methods to the adsorption capacity data. These adsorption capacity dataset has been constructed by the implementation of the Langmuir equation applying the model parameters obtained by Heller and Zoback lab experience. More encouraging outcomes might be obtained if the linear regression fitting is applied directly to experimental results.

5. Conclusions and possible Future Works

This study describes multi-component sorption mechanisms in shale matrix under time dependent conditions. The kerogen-inorganic shale matrix is a material with a high content of nano-pores. In order to describe the gas flux through the shale domain, two gas transport mechanism have been considered: molecular diffusion and Knudsen diffusion. It could be stated that the Knudsen diffusion has a big impact on gas flux due the nano-pore structure of the shale matrix.

Regarding the adsorption mechanisms, the study has successfully compared three of the most popular adsorption models. It could be stated that the Freundlich isotherm gives fairly similar results than the Langmuir approach. Moreover, the Freundlich isotherm is not restricted to monolayer formation, an important aspect that several authors have put in doubt related to CO_2 adsorption in shale reservoirs. Regarding the BET isotherm, results are far from the expected. However, it should be considered that the simulation conditions are not exactly the ones required for multilayer conditions.

Finally, it is recommended that this work could be continued by including other phenomena such as the effect of water on CH_4 or CO_2 adsorption in shale. Laboratory tests with the aim of measuring the adsorption capacity at different level of water content, like the experience performed by Feng et al., should be also performed in shale samples.

6. References

Akkutlu, I. Y. and Fathi, E., "Multiscale Gas Transport in Shales with Local Kerogen Heterogeneities." *Society of Petroleum Engineers (SPE) Journal*, **17**, 1-002 (2012).

EPA, US Environmental Protection Agency. "Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990:2016." Washington D.C. (2016).

Fathi, E. and Akkutlu, I. Y., "Mass Transport of Adsorbed-phase in Stochastic Porous Medium with Fluctuating Porosity Field and Nonlinear Gas Adsorption Kinetics." *Transport in Porous Media*, **91**, 5-33 (2012).

Feng, D., Li, X., Wang, X., Jing Li, Sun, F., Sun, Z., Zhang, T., Li, P., Chen, Y. and Zhang, X., "Water Adsorption and its Impact on the Pore Structure Characteristics of Shale Clay", *Applied Clay Science*, **155**, 126-138 (2018).

Foo, K. Y. and Hammed, B. H. "Insights into the Modeling of Adsorption Isotherm Systems." *Chemical Engineering Journal*, **156**, 2-10 (2010).

Heller, R. and Zoback, M., "Adsorption of Methane and Carbon Dioxide on Gas Shale and Pure Mineral Samples." *Journal of Unconventional Oil and Gas Resources*, **8**, 14-24 (2014).

Jin, Z. and Firoozabadi, A., "Effect of Water on Methane and Carbon Dioxide Sorption in Clay Minerals by Monte Carlo Simulations." *Fluid Phase Equilibria*, **382**, 10-20 (2014).

Kang, S. M., Fathi, E., Ambrose, R. J., Akkutlu, I. Y. and Sigal, R. F., "Carbon Dioxide Storage Capacity of Organic-Rich Shales." *SPE Journal*, **16**, 842-855 (2011).

Mengal, S. and Wattenbarger, R., "Accounting for adsorbed gas in shale gas reservoirs." *Society of Petroleum Engineers (SPE) Middle East Oil & Gas Show and Conference (2011).*

Prajapati, N. J. and Mills, P. L. "Numerical Study of Flux Models for CO_2: Enhanced Natural Gas Recovery and Potential CO_2 Storage in Shale Gas Reservoirs." *COMSOL Annual Conference.* Boston (2014).

Solsvik, J. and Jakobsen, H. A. "Mathematical Modeling of Multicomponent Mass Diffusion in Porous Pellets: Mass and Molar formulations." *Energy Procedia*, **26**, 107-115 (2012).

Sun, H., Yao, J., Gao, S., Fan, D., Wang, C. and Sun, Z., "Numerical Study of CO_2 Enhanced Natural Gas Recovery and Sequestration in Shale Gas Reservoirs." *International Journal of Greenhouse Gas Control*, **19**, 406-419 (2013).