COMSOL
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Simulation of Adsorption Mechanisms of CH_4 and CO_2 in Shale matrix

Session: Chemical Engineering

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Outline

- Introduction .... (3)
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Introduction

- According to the Environmental Protection Agency (EPA), CO2 is the major contributor to greenhouse gas (GHG) emission in the US and worldwide, phenomenon that is considered responsible for global warming trends.

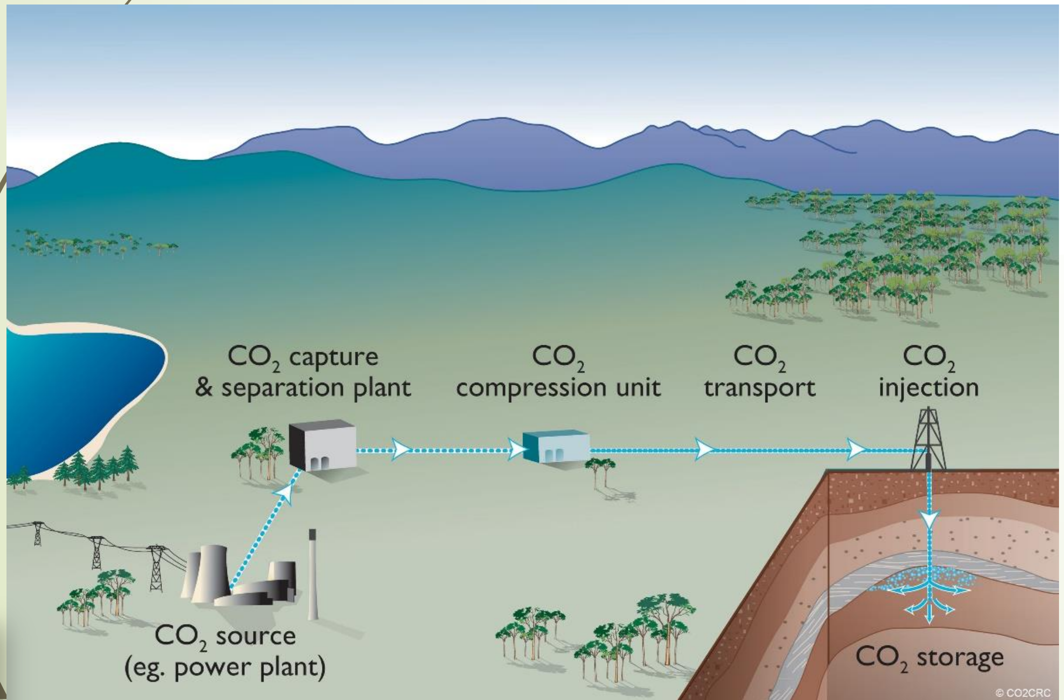
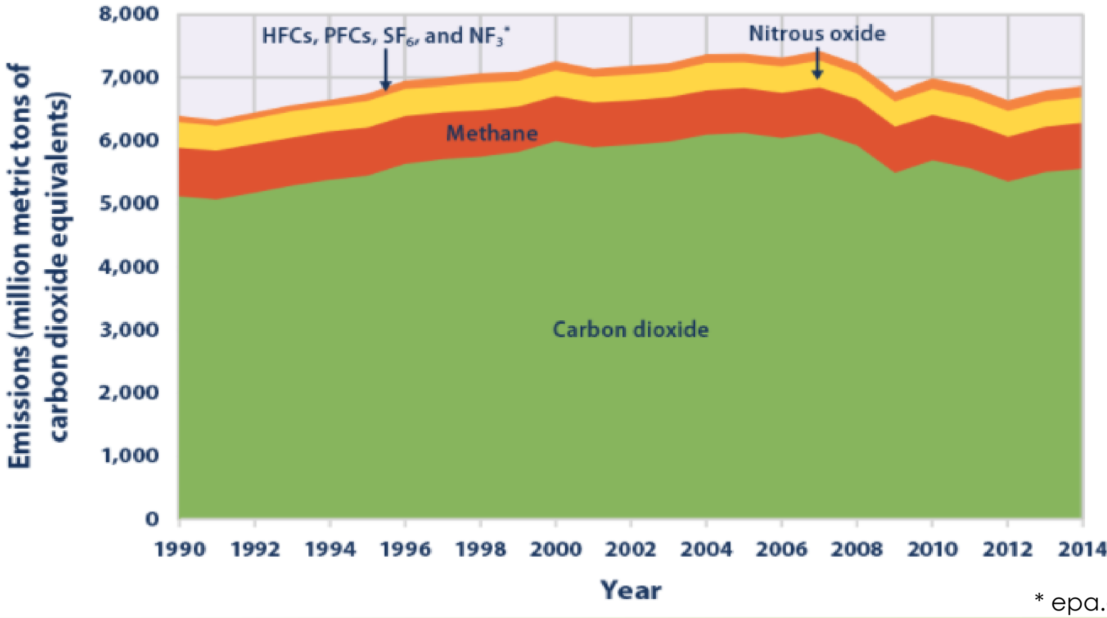


Figure 1. U.S. Greenhouse Gas Emissions by Gas, 1990–2014



* epa.gov

- Carbon Capture & Storage (CCS) is considered as one of the main actions to be implemented to mitigate climate change effects (IPCC, 2014).

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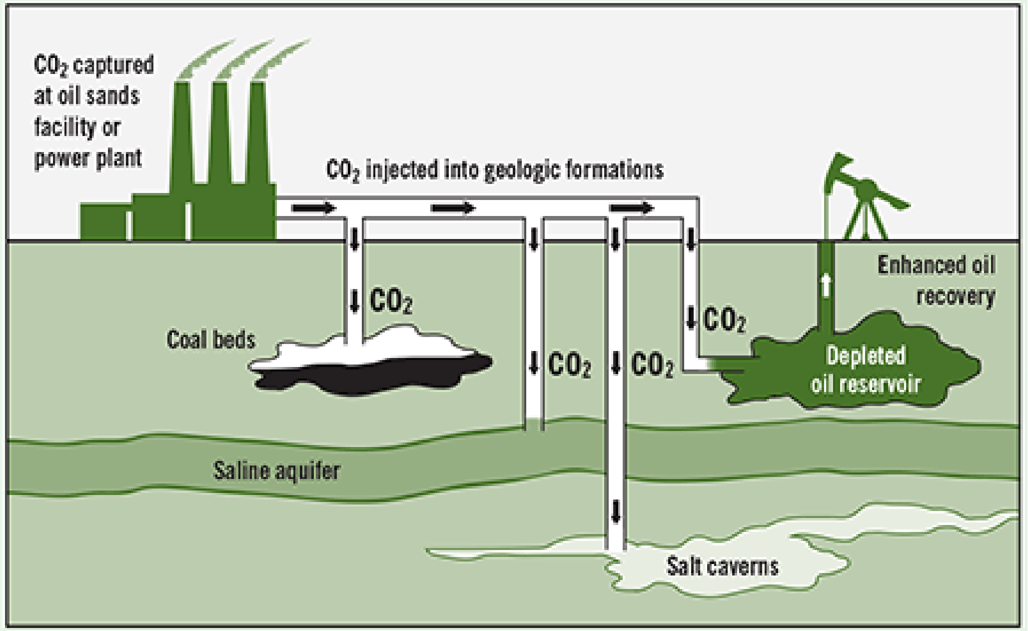
Geological Storage of CO_2



- Main types of formation reservoirs to consider as a potential CO_2 storage site:

1) Coal beds.
2) Saline formations.
3) Basalts.
4) Oil & Gas reservoirs:

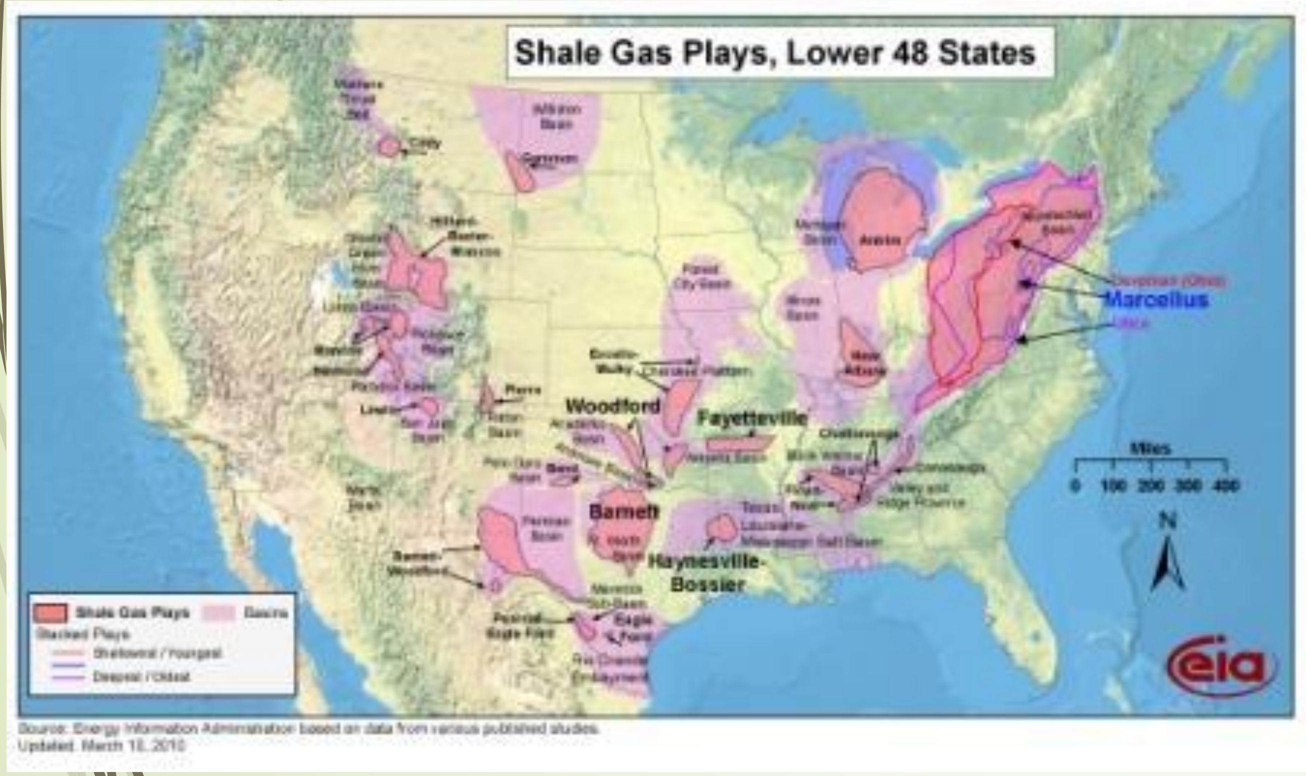
- ➢ Conventional Oil & Gas Reservoirs.
- ➢ Unconventional Oil & Gas Reservoirs (Shale).

- ☐ CCS is considered to be an expensive technique. The synergy with other commercial activities (like oil & gas production) is essential for CCS deployment.
- ☐ CO_2 injection for enhance oil/gas recovery (EOR/EGR) meets two main goals:
- ✓ Mitigate CO_2 emissions to the atmosphere.
- ✓ Increase hydrocarbon (HC) production and reserves.

Introduction

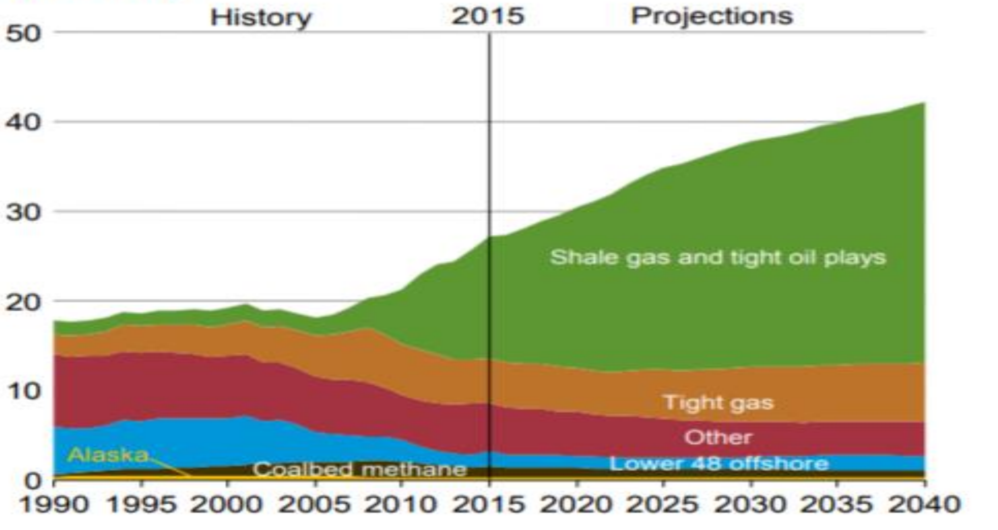
Shale Reservoirs:

❑ Shale reservoirs in general have:
- Low porosity.
- Ultra-low permeability.
- Heterogeneous chemical composition.



Source: Energy Information Administration based on data from various published studies.
Updated: March 10, 2010

Figure ES-7. U.S. dry natural gas production by source in the Reference case, 1990–2040 (trillion cubic feet)



* EIA 2016

- Technology improvements achieved in the last decades in Hydraulic Fracturing and Horizontal Drilling have incredibly increased HC extraction from shale reservoirs.

Motivation

- **Contribute to the development of CCS** techniques. By **injecting CO_2 for EOR/EGR**, we can increase oil & gas production while also taking CO_2 molecules out from the atmospheric carbon cycle.
- **Shale reservoirs** are playing a **key role in HC production**. These reservoirs decrease their production in relatively short period of time. CO_2 injection in shale reservoirs would help to increase HC recovery from these formations.
- Studies show that **sorption processes have a great impact on CH_4 production from shale reservoirs** (*Yu and Sepehrnoori,* 2013) **as well as for CO_2 storage** in these type of formations (*Kang et al.,* 2011).
- Detailed comparison about different CO_2 and CH_4 adsorption models on shale reservoirs have not been extensively covered.

Relevant Literature Review

- *"Adsorption of CH_4 and CO_2 on gas shale and pure minerals samples"*
  (*R. Heller and M. Zoback*, 2013). → Lab tests, dry conditions. Langmuir fitting.
  CO_2 2-3 times higher adsorption capacity than CH_4.
- *"CH_4 and CO_2 adsorption in clay-like slit pores by Monte Carlo simulations"*
  (Z. Jin and A. Firoozabadi, 2013). → Molecular simulation. Langmuir fitting.
  Cation exchange affects CO_2 sorption.
- "Effect of H_2O on *CH_4 and CO_2 sorption in clay minerals by Monte Carlo simulations*"
  (Z. Jin and A. Firoozabadi, 2014). → H_2O significantly reduces CO_2 and CH_4 sorption.
  CO_2 may form multilayer adsorption at high pressure.
- *"Numerical study of CO_2 EUR and sequestration in shale gas reservoirs"*
  (H. Sun et *al.*, 2013). → **COMSOL simulation**. **Darcy's law not applicable for flow in shales.**
  Knudsen diffusion, ordinary diffusion and dual-porosity model needed.
- *"Numerical study of flux models for CO_2: EUR and potential CO_2 storage in shale gas reservoirs"*
  (N. Prajapati and P. Mills, 2014). → **COMSOL simulation**. CO_2 flow in shale fitted to different flux models coupled with Langmuir adsorption model. **Nano-pore have high impact in gas flux.**
- "H_2O adsorption and its impact on the pore structure characteristics of shale clay"
  (D. Feng et *al.*, 2018). → **Lab tests, N_2 adsorbed in clays at different HR.**
  GAB model gives optimal fitting parameters for H_2O adsorption.

Research Objective

- **Simulate both, gas flow** from the induced fracture to the shale particle surface **and adsorption processes** in order to get a better understanding of what happens in subsurface when CO_2 is injected.

- The **focus** of this study will be **on modeling CO_2 and CH_4 sorption mechanisms** in shale drained matrix.

System Description

Assumptions:

- Ideal gas behavior.
- Single-phase gas flow.
- Constant reservoir T.
- Constant rock compressibility.
- Isotropic and homogeneous matrix.

Main parameters	
Porosity	8%
Permeability (m2)	1.0E-19
Rock density (kg/m3)	2560
Rock compressibility (1/Pa)	1.0E-05
Tortuosity	4
Reservoir Temperature (K)	353
Pore diameter (nm)	20
Molecular Diffusion (cm2/s)	1.0E-08
Initial Pressure (Pa)	2.5E+06
Injection Pressure (Pa)	1.0E+07

* Sun *et al.* (2013)

☐ Continuity equation:

Accumulation + Flux in – Flux out = 0

$$\frac{\partial \rho}{\partial t} + \nabla.(\rho.u) = 0$$

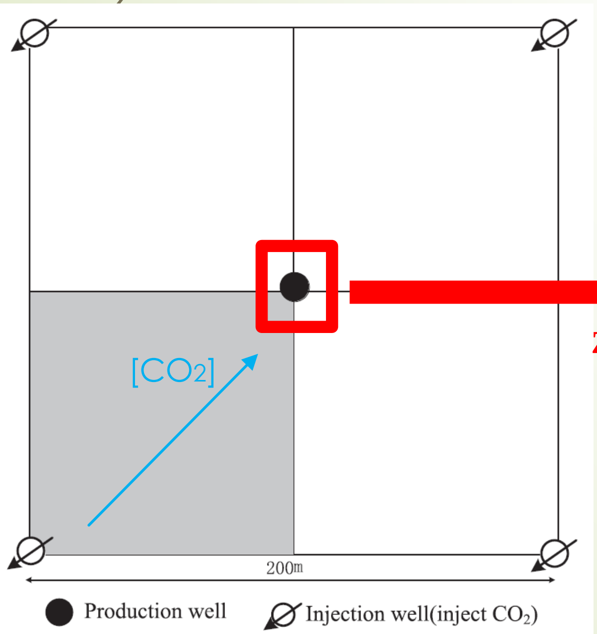
- *Initial Condition*

$$P_{m,i}(x,y,t)_{t=0} = P_{initial}$$

- *Boundary Conditions*

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

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



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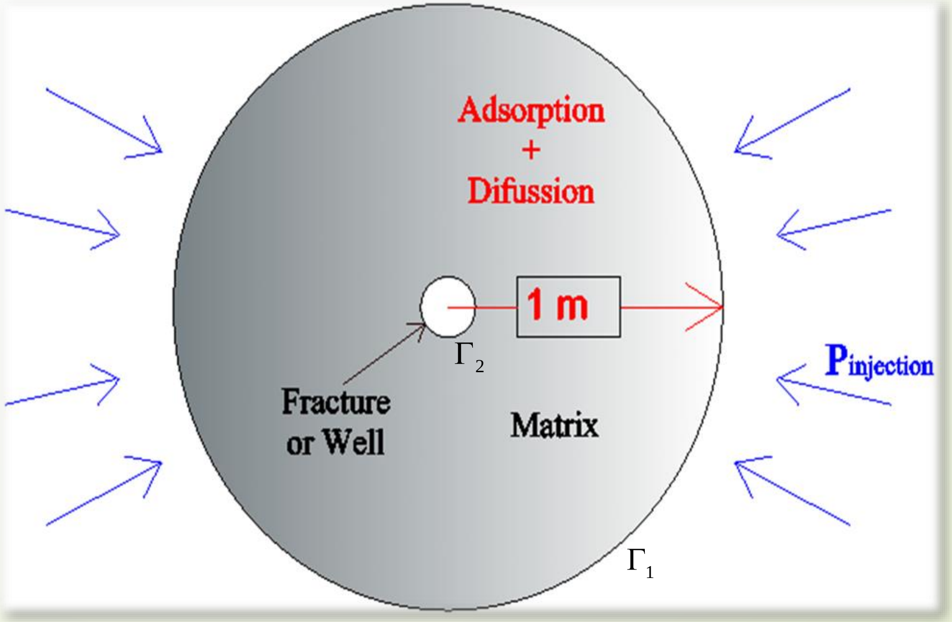


☐ COMSOL Settings:

- Transport of Diluted Species in Porous Media module.
- Time dependent PARDISO Solver
- Tolerance Factor: 0.1
- Iterative Steps: 5

Governing Multiphysics Equations

- **Shale matrix Specie Mass Balance**

$$\frac{\partial\left(\rho.\phi_m + \rho_q.(1-\phi_m)\right)}{\partial t} + \nabla.(\rho.u)_{m,i} = 0$$

For CH4, *i* = 1.
For CO2, *i* = 2.

$$\rho_i = \frac{P_i M_i}{Z_i RT} \qquad P_i = x_i.P \qquad \rho_{q,i} = \frac{\rho_s M_i}{V_{std}} \times q_{ads,i}$$

Adsorbed gas density

- **Flux Model:**

Wilke Model:

$$N_i = -D_{ei,m}.\nabla C_i \qquad D_{ei,m} = \frac{1}{\sum\limits_{\substack{j=1\\ j\neq i}}^{n}\left(x_j / D^e_{ij}\right)}$$

Wilke-Bosanquet Model:

$$N_i = \left(-D_{i,eff}.\nabla C_i\right) \qquad \frac{1}{D_{i,eff}} = \frac{1}{D_{ei,m}} + \frac{1}{D^e_{k_i}}$$

$$D_{ei,k} = \frac{\phi_m}{\tau}.\frac{d_{pore}}{3}.\sqrt{\frac{8RT}{\pi.M_i}}$$

- **Adsorption Models:**

Monolayer Adsorption → *Langmuir Isotherm:*

$$q_{ads,i} = \frac{V_{L,i}.B_i.P_i}{1 + B_i.P_i} \qquad B_i = \frac{1}{P_{L,i}}$$

Not restricted to formation of Monolayer → *Freundlich Isotherm:*

$$q_{ads,i} = K_F.P_i^{1/n}$$

→ Does not approach Henry's Law at low concetration

Brunauer-Emmett-Teller (BET) Isotherm:

Multilayer Adsorption →

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

Expressed in concentration →

$$q_{ads,i} = \frac{q_s *.C_{BET}.\left({}^{C_i}/_{C_s}\right)}{\left(1-\left({}^{C_i}/_{C_s}\right)\right)\left[1+(C_{BET}-1).\left({}^{C_i}/_{C_s}\right)\right]}$$

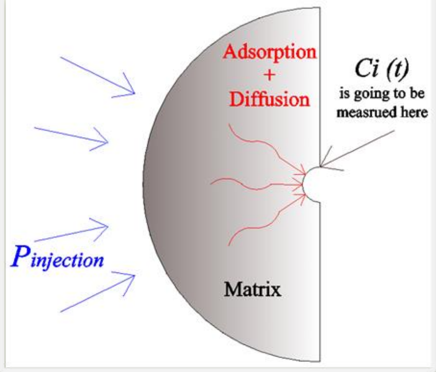
GAB Isotherm. Feng *et al.* (2018) →

$$q_{ads,i} = \frac{q_{sat_{mono}}.C_{mono_{heat}}.\left(k_{multi_{heat}}.x\right)}{\left(1-\left(k_{multi_{heat}}.x\right)\right)\left[1+\left(C_{mono_{heat}}-1\right).\left(k_{multi_{heat}}.x\right)\right]}$$

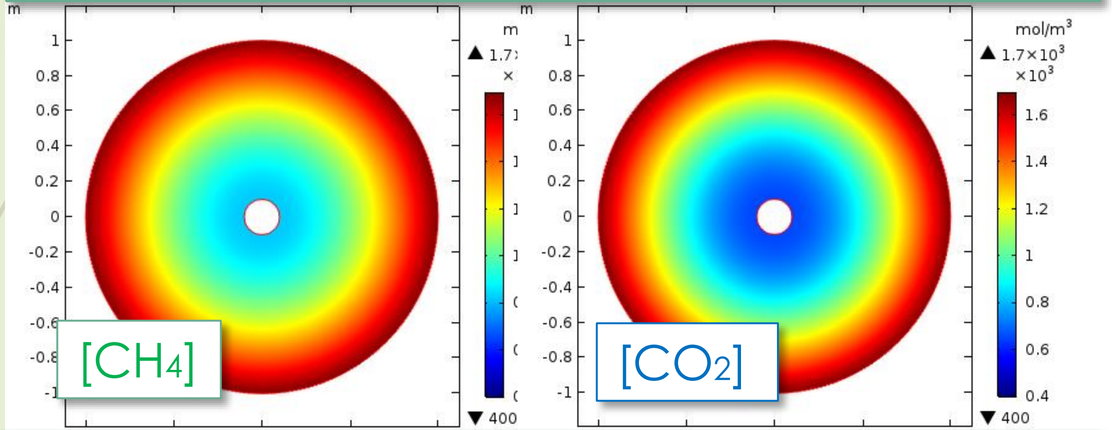
Results and Discussion

Langmuir Adsorption + Wilke Flux model

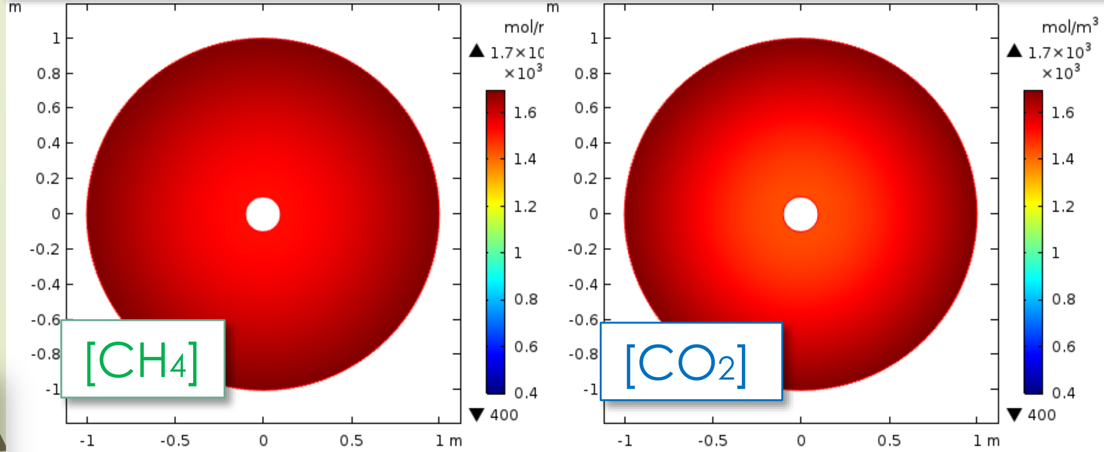
$$q_{ads,i} = \frac{V_{L,i}.B_i.P_i}{1 + B_i.P_i} \qquad + \qquad N_i = -D_{ei,m}.\nabla C_i \qquad D_{ei,m} = \frac{1}{\sum_{\substack{j=1 \\ j\neq i}}^{n} \left(x_j / D_{ij}^{e} \right)}$$



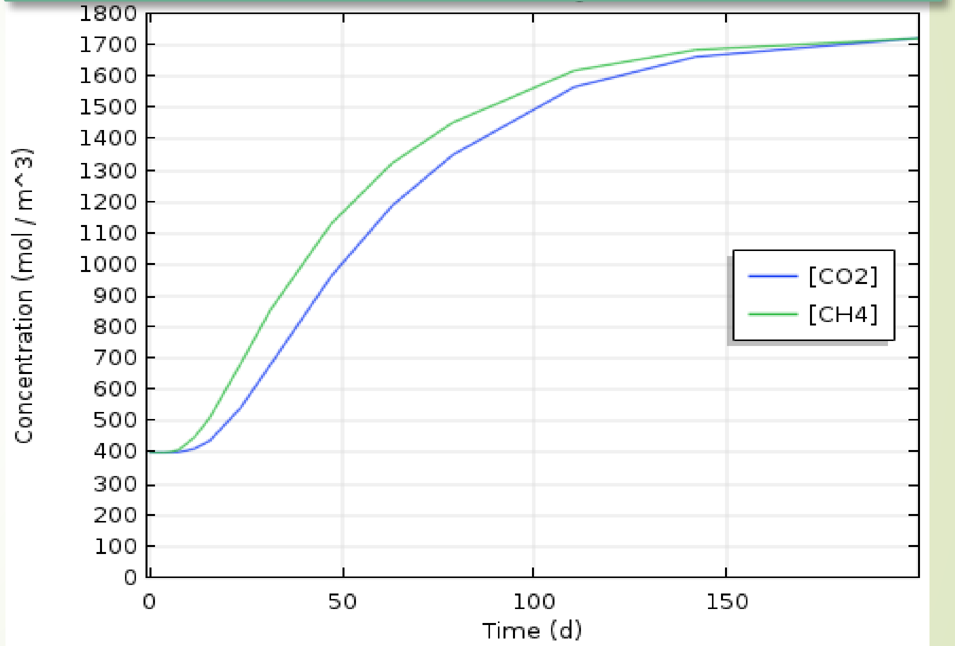
Injection Time = 30 days



Injection Time = 90 days



Concentration vs. Time



Langmuir parameters

$V_{L,\ CH4}$	Langmuir volume of CH4 (std.ft^3/kg)	1.27E-02
$V_{L,\ CO2}$	Langmuir volume of CO2 (std.ft^3/kg)	3.31E-02
$P_{L,\ CH4}$	Langmuir pressure of CH4 (psi)	694.7
$P_{L,\ CO2}$	Langmuir pressure of CO2 (psi)	409.6

* Heller and Zoback (2014)

Results and Discussion

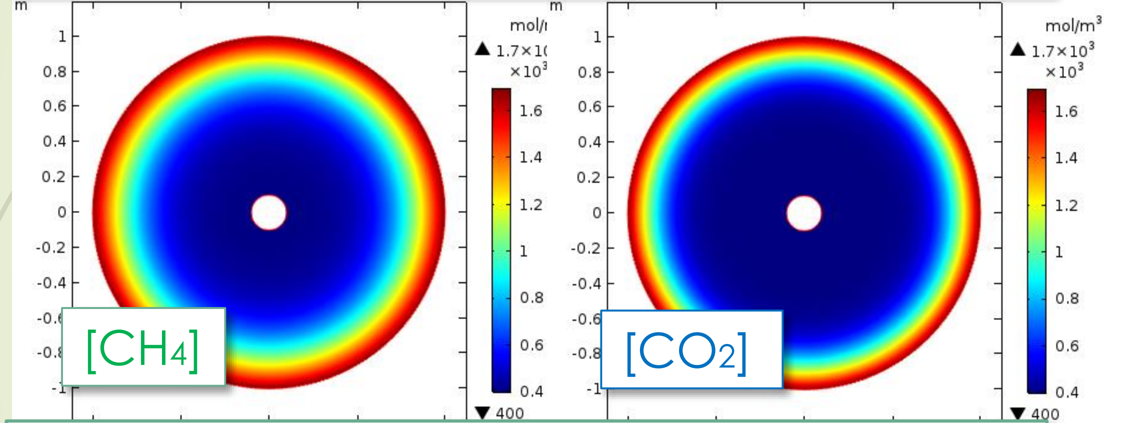
Langmuir Adsorption + Wilke-Bosanquet Flux model

$$q_{ads,i} = \frac{V_{L,i}.B_i.P_i}{1 + B_i.P_i} \quad + \quad N_i = \left(-D_{i,eff}.\nabla C_i\right)$$

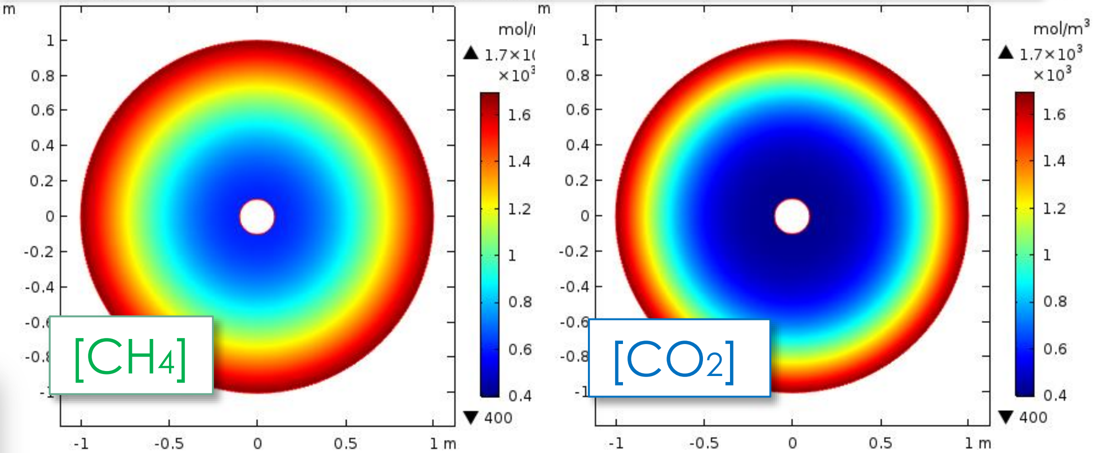
$$\frac{1}{D_{i,eff}} = \frac{1}{D_{ei,m}} + \frac{1}{D^e_{k_i}}$$

$$D_{ei,m} = \frac{1}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \left(x_j / D^e_{ij} \right)}$$

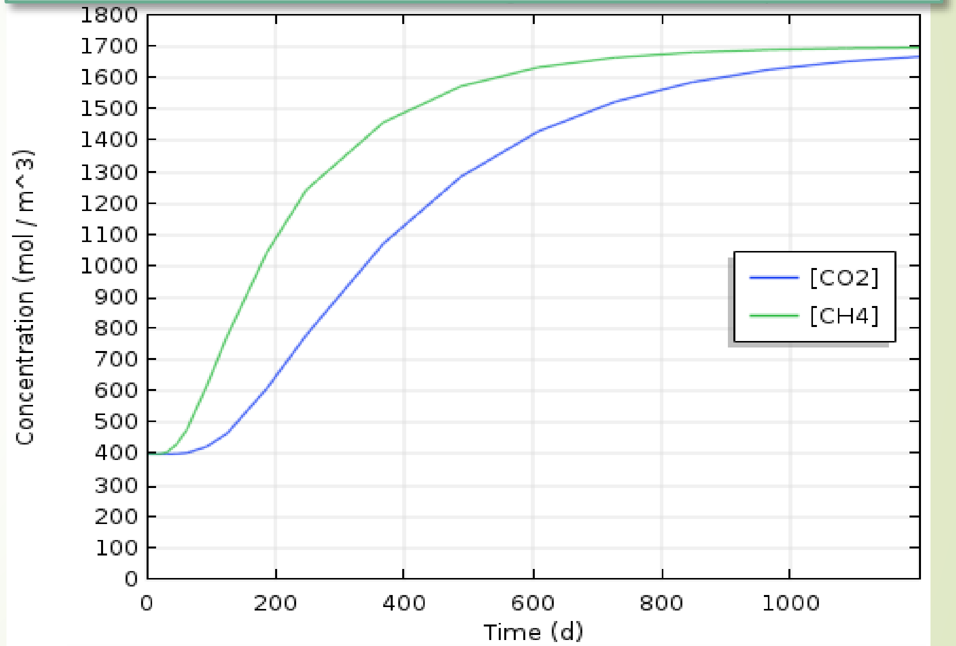
Injection Time = 30 days



Injection Time = 90 days



Concentration vs. Time



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* Heller and Zoback (2014)

Results and Discussion

Wilke vs. Wilke-Bosanquet Flux model

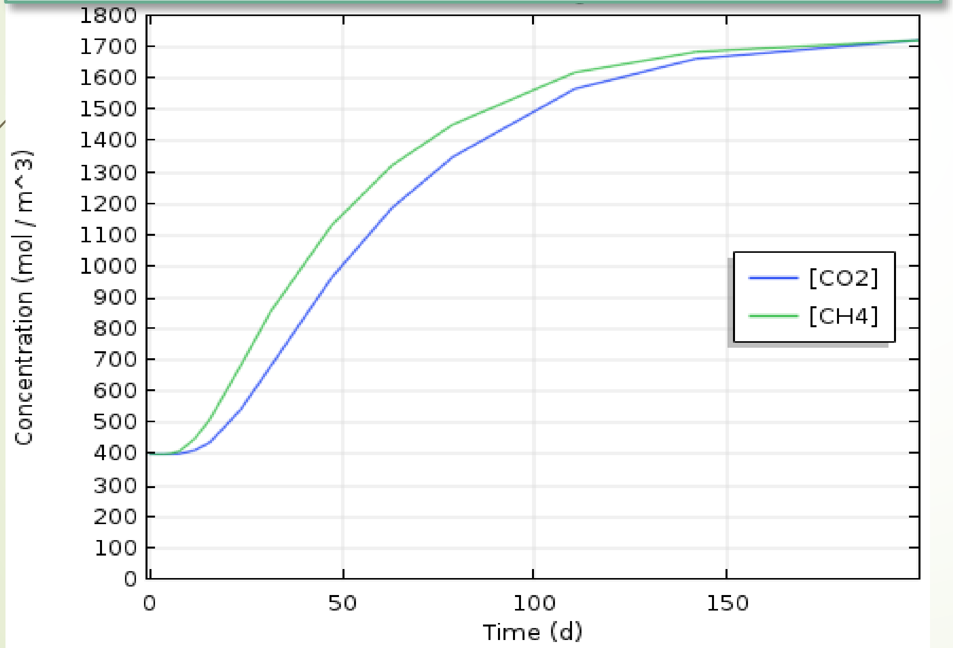
- **Adsorption Model:**
  Langmuir Isotherm

$$N_i = -D_{ei,m}.\nabla C_i \qquad D_{ei,m} = \frac{1}{\sum_{\substack{j=1\\ j\neq i}}^{n} \left(x_j \big/ D^e_{ij} \right)}$$

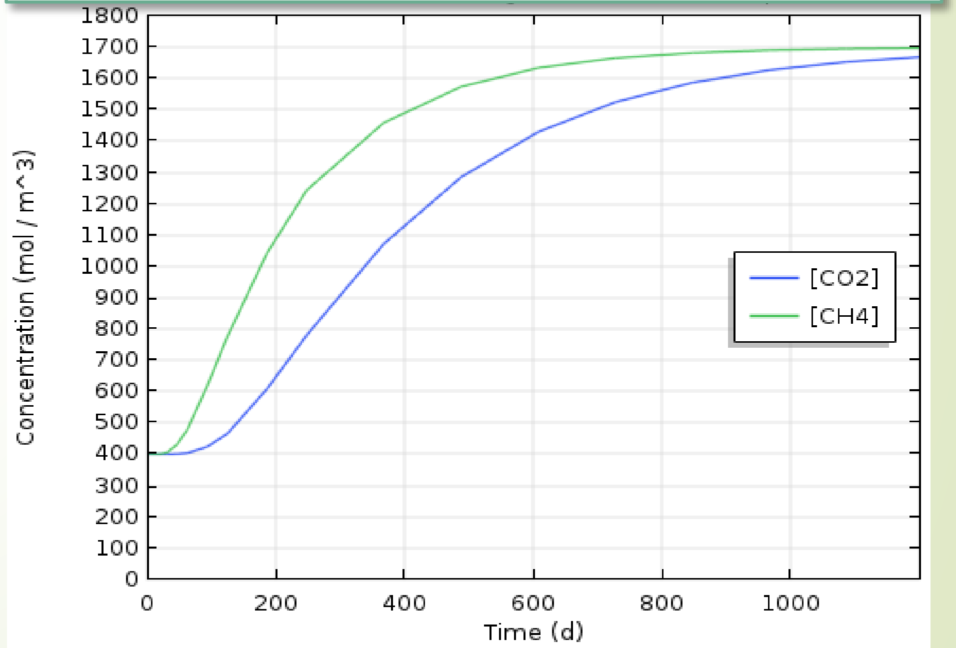
$$N_i = \left(-D_{i,eff}.\nabla C_i\right) \qquad \frac{1}{D_{i,eff}} = \frac{1}{D_{ei,m}} + \frac{1}{D^e_{k_i}}$$

$$D_{ei,m} = \frac{1}{\sum_{\substack{j=1\\ j\neq i}}^{n} \left(x_j \big/ D^e_{ij} \right)}$$

Wilke Flux model



Wilke-Bosanquet Flux model



- **Wilke-Bosanquet flux is much smaller** than Wilke flux model (**due to shale nano-pores**).

Results and Discussion

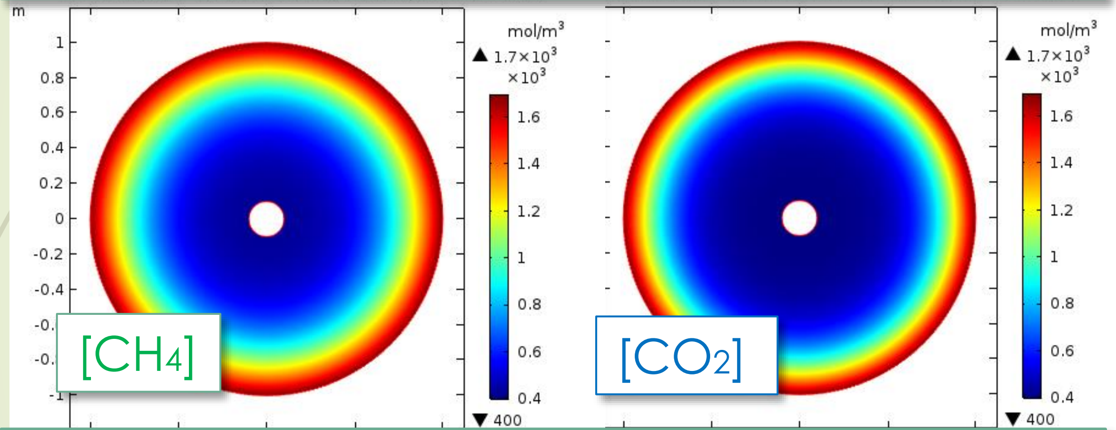
Freundlich Adsorption + Wilke-Bosanquet Flux model

$$q_{ads,i} = K_F . P_i^{1/n} \quad + \quad N_i = \left(-D_{i,eff} . \nabla C_i\right)$$

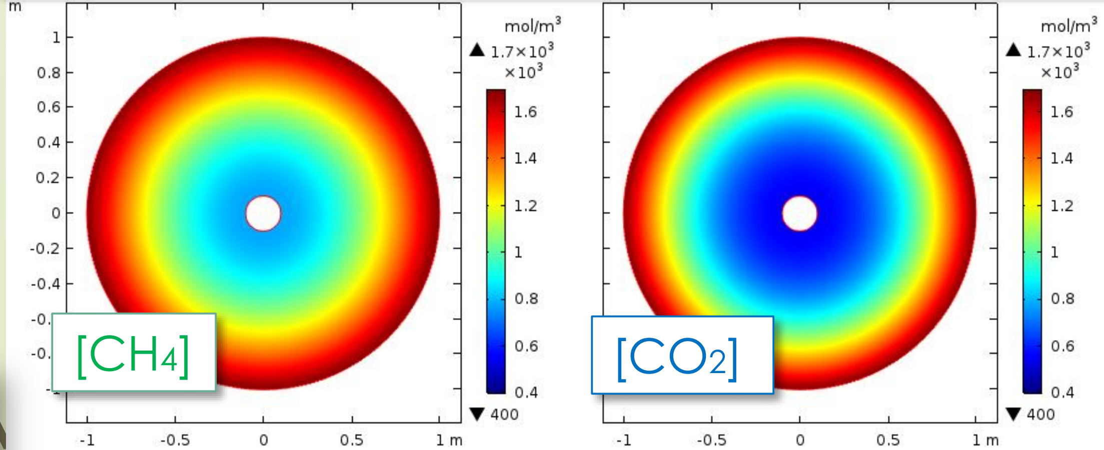
$$\frac{1}{D_{i,eff}} = \frac{1}{D_{ei,m}} + \frac{1}{D^e_{k_i}}$$

$$D_{ei,m} = \frac{1}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \left(x_j \middle/ D^e_{ij} \right)}$$

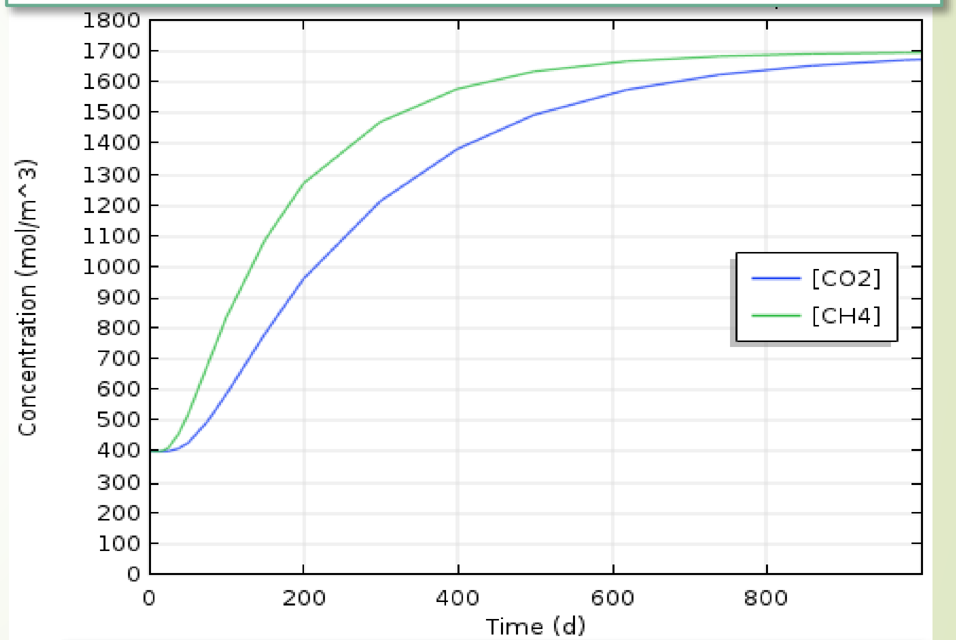
Injection Time = 30 days



Injection Time = 90 days



Concentration vs. Time



Freundlich parameters

$K_{F,\ CH_4}$	Freundlich adsorption constant for CH4 (mol/kg)	1.105E-04
$K_{F,\ CO_2}$	Freundlich adsorption constant for CO2 (mol/kg)	6.145E-05
n_{CH_4}	Freundlich adsorption exponent for CH4	2.114
n_{CO_2}	Freundlich adsorption exponent for CO2	1.503

* Computed with data from Heller and Zoback (2014)

Results and Discussion

Langmuir vs. Freundlich Adsorption model

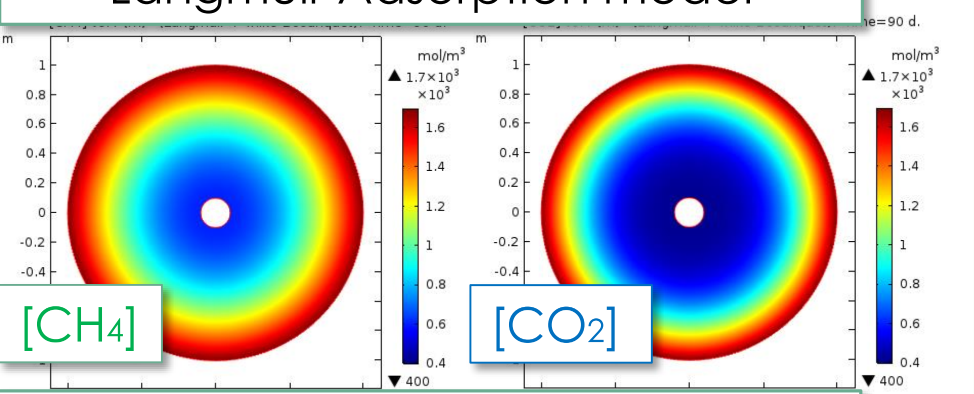
- **Flux Model:**

  Wilke-Bosanquet

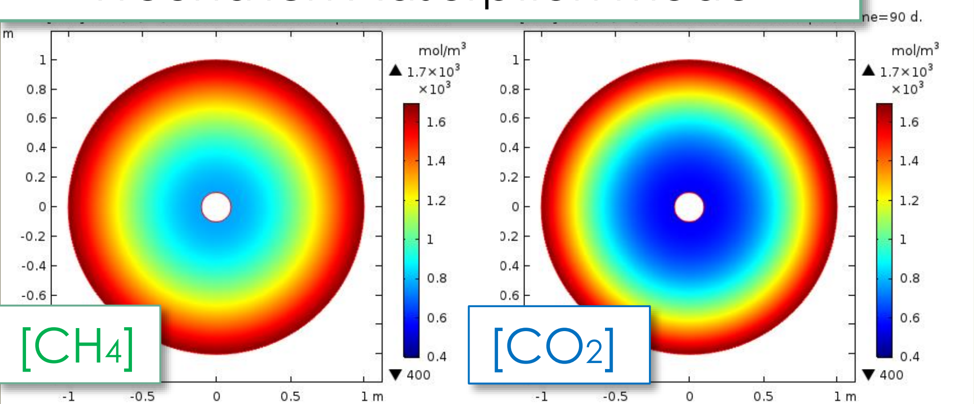
$$q_{ads,i} = \frac{V_{L,i}.B_i.P_i}{1 + B_i.P_i} \qquad q_{ads,i} = K_F.P_i^{1/n}$$

- **At 90 days of Injection:**

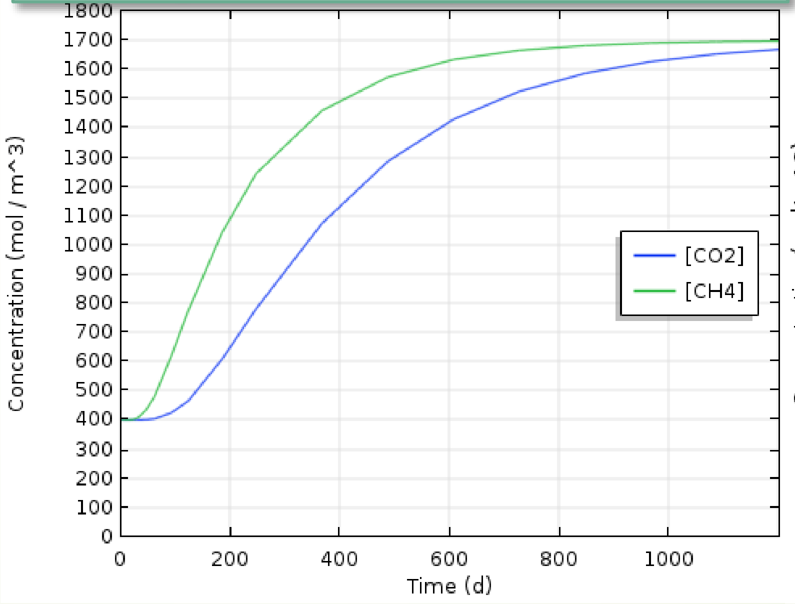
Langmuir Adsorption model



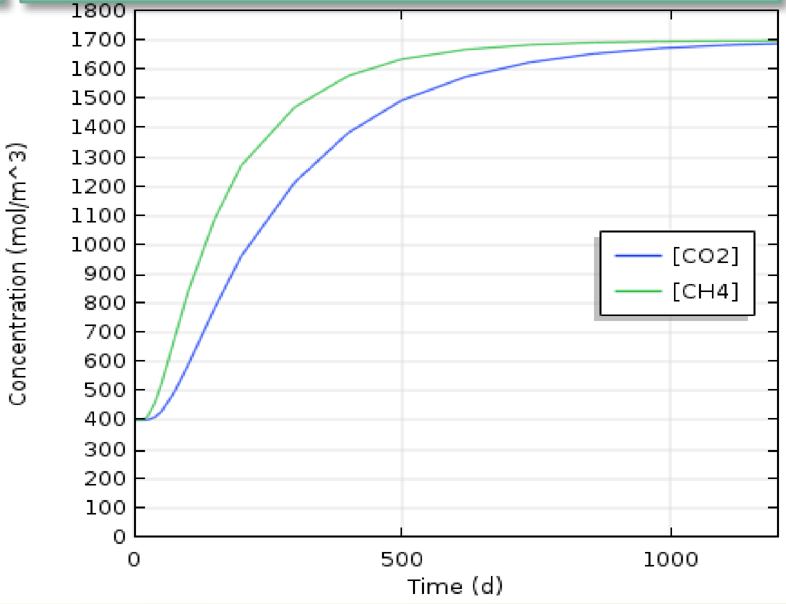
Freundlich Adsorption model



Langmuir Adsorption model



Freundlich Adsorption model



- After aprox. 800 days, both models provide similar results.

Langmuir vs. BET Adsorption model

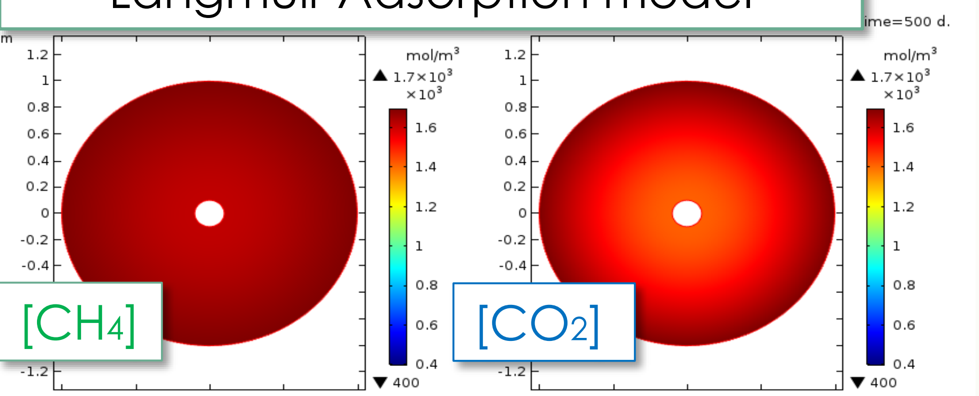
- **Flux Model:**
  Wilke-Bosanquet

$$q_{ads,i} = \frac{V_{L,i}.B_i.P_i}{1 + B_i.P_i}$$

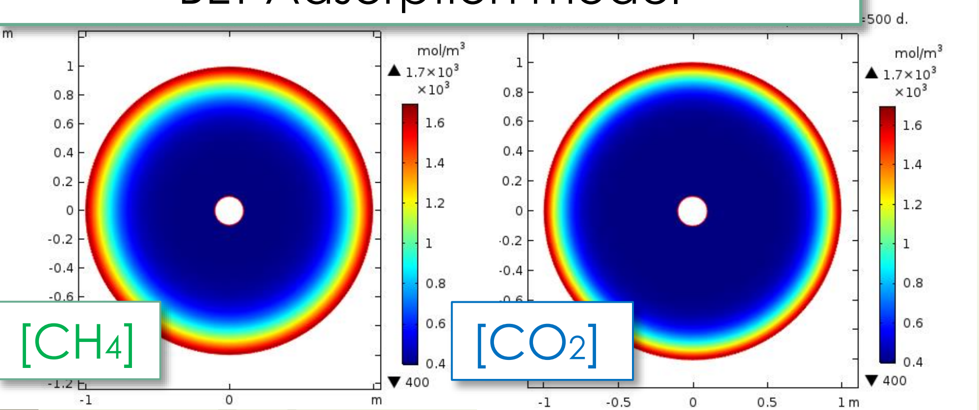
$$q_{ads,i} = \frac{q_s.P_{BET}.P_i}{(P_s - P_i)\left[1 + (P_{BET} - 1)\left({P_i}/{P_s}\right)\right]}$$

- **At 500 days of Injection:**

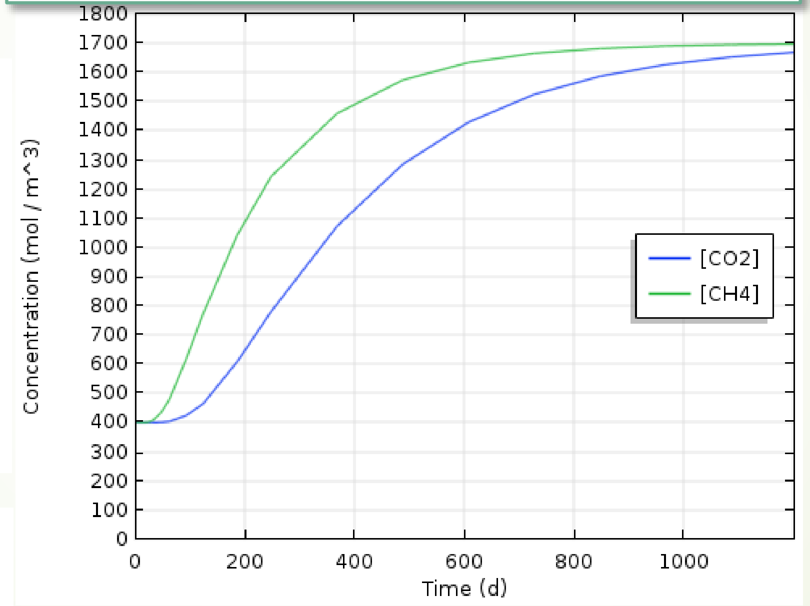
Langmuir Adsorption model



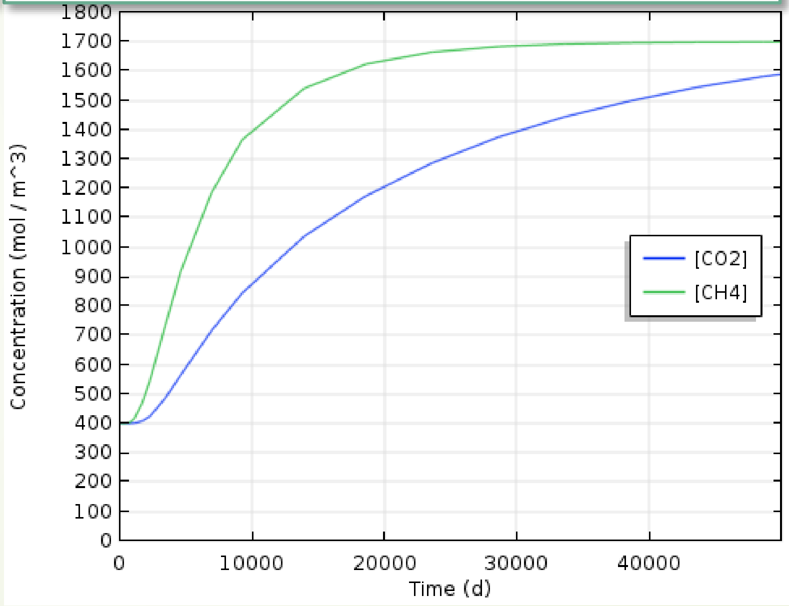
BET Adsorption model



Langmuir Adsorption model



BET Adsorption model



BET parameters

$q_{s,CH4}$	BET Isotherm saturation capacity for CH4 (mol/kg)	5.433E-03
$q_{s,CO2}$	BET Isotherm saturation capacity for CO2 (mol/kg)	1.155E-02
$P_{BET,CH4}$	BET adsorption pressure of CH4	26.7
$P_{BET,CO2}$	BET adsorption pressure of CO2	43.8
$P_{s,CH4}$	Saturation pressure of CH4 (psi)	2500
$P_{s,CO2}$	Saturation pressure of CO2 (psi)	1100

* Computed with data from Heller and Zoback (2014)

Conclusions

- Comparison of flux models shows that **Knudsen diffusion has a great relevance in gas flow due to presence of nano-pores** in shale matrix.

- Comparison of **Langmuir and Freundlich adsorption models** shows that both models **provide similar results**. Small deviation is found at low pressures. Therefore, it could be concluded that Freundlich model could be used for modeling gas adsorption in shale under conditions where the monolayer formation is not guaranteed.

- Sensitivity analysis proves that reservoir characterization has great importance for a correct simulation of the flux model.

Possible Future Work

- **BET adsorption modeling did not provide the expected results**. However, it should be considered that simulation conditions were not exactly the ones necessary for multilayer formation.

- This work can be extended by including other phenomena such as water effect on CH_4 or CO_2 adsorption in shale. **Laboratory tests in shale samples with the aim of measuring the adsorption capacity at different water content should be performed.**

Thanks!

Questions?

Construction of Adsorption Set Database

- From experimental results from Heller and Zoback (2014):

Langmuir parameters		
$V_{L,\,CH_4}$	Langmuir volume of CH4 (std.ft^3/kg)	1.27E-02
$V_{L,\,CO_2}$	Langmuir volume of CO2 (std.ft^3/kg)	3.31E-02
$P_{L,\,CH_4}$	Langmuir pressure of CH4 (psi)	694.7
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+

$$q_{ads,i} = \frac{V_{L,i}.B_i.P_i}{1 + B_i.P_i}$$

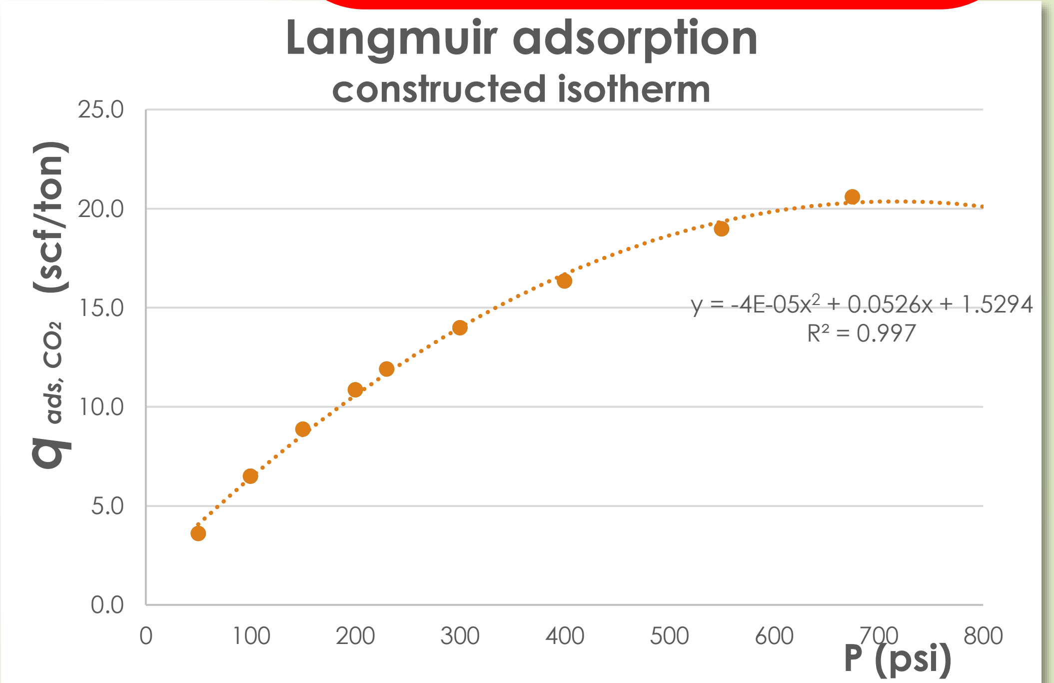
+

- Assuming component partial pressure:

P (psia)
675
550
400
300
230
200
150
100
50

P (psia)	$q_{ads,\,CO_2}$ (scf/ton)
675	20.60
550	18.97
400	16.35
300	13.99
230	11.90
200	10.86
150	8.87
100	6.50
50	3.60

Constructed database



Obtention of Freundlich parameters

Constructed database

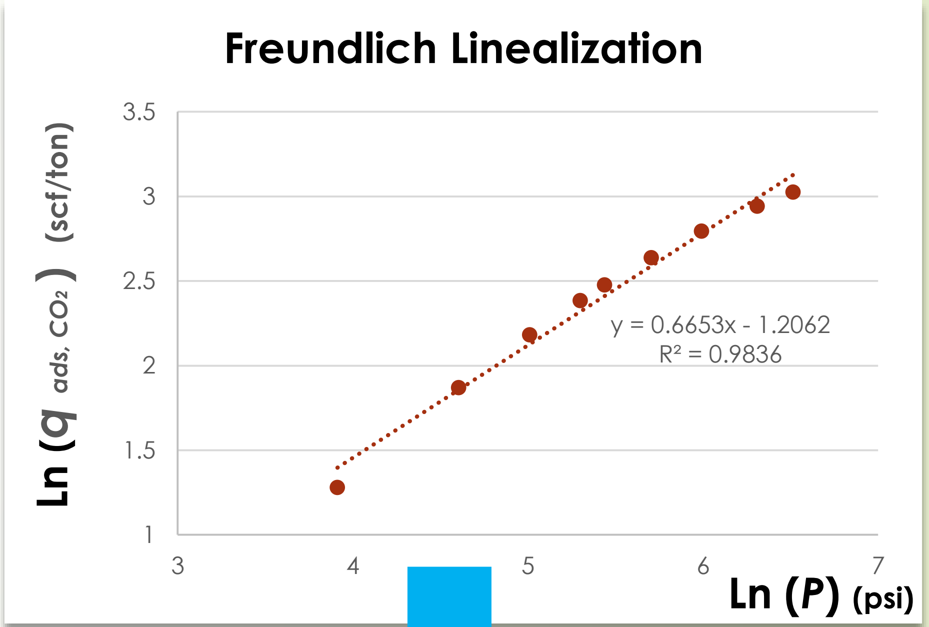
P (psia)	$q_{ads,\ CO_2}$ (scf/ton)
675	20.60
550	18.97
400	16.35
300	13.99
230	11.90
200	10.86
150	8.87
100	6.50
50	3.60

+

$$q_{ads,i} = K_F . P_i^{1/n}$$

Linearization

$$Ln(q_{ads,CO_2}) = Ln(K_F) + \left(\frac{1}{n}\right) * Ln(P)$$



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n_{CO2}	Freundlich adsorption exponent for CO2	1.503

Obtention of BET parameters

Constructed database

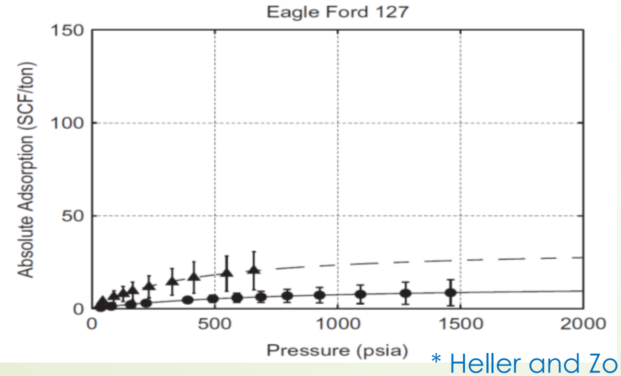
P (psia)	$q_{ads,\,CO_2}$ (scf/ton)
675	20.60
550	18.97
400	16.35
300	13.99
230	11.90
200	10.86
150	8.87
100	6.50
50	3.60

+

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

+

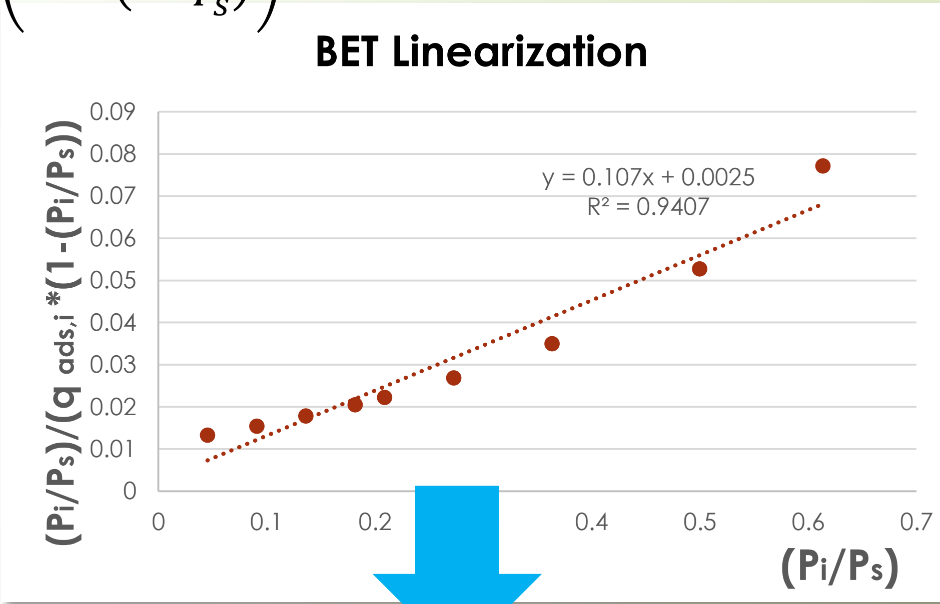
- Assuming saturation pressure (P_s):



* Heller and Zoback (2014)

Linearization

$$\frac{\left({}^{P_i}/_{P_s}\right)}{q_{ads,i}\cdot\left(1-\left({}^{P_i}/_{P_s}\right)\right)} = \frac{1}{q_s.P_{BET}} + \left[\frac{(P_{BET}-1)}{q_s.P_{BET}}\right].\left({}^{P_i}/_{P_s}\right)$$



BET parameters

$q_{s,\,CH_4}$	BET Isotherm saturation capacity for CH4 (mol/kg)	5.433E-03
$q_{s,\,CO_2}$	BET Isotherm saturation capacity for CO2 (mol/kg)	1.155E-02
$P_{BET,\,CH_4}$	BET adsorption pressure of CH4	26.7
$P_{BET,\,CO_2}$	BET adsorption pressure of CO2	43.8
$P_{s,\,CH_4}$	Saturation pressure of CH4 (psi)	2500
$P_{s,\,CO_2}$	Saturation pressure of CO2 (psi)	1100