Exploring the Behavior of Shales as Seals and Storage Reservoirs for CO_2

Project Number 90210

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U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and
Infrastructure for CCS

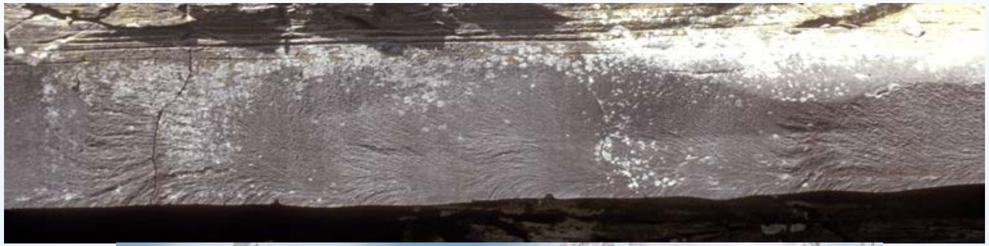
August 12-14, 2014

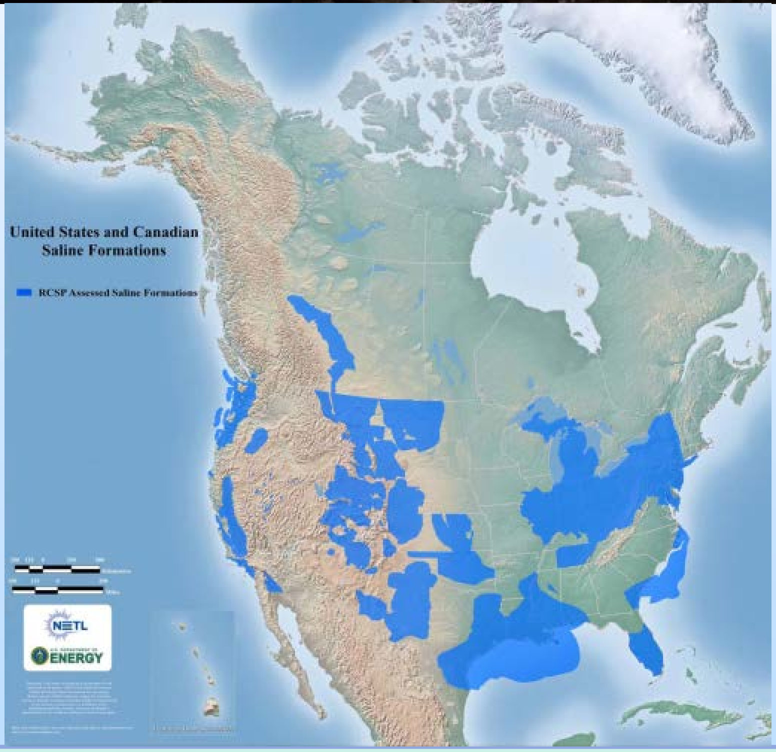
Presentation Outline

- Benefits to Program
- Project Goals and Objectives
- Technical Status
- Accomplishments to Date
- Summary

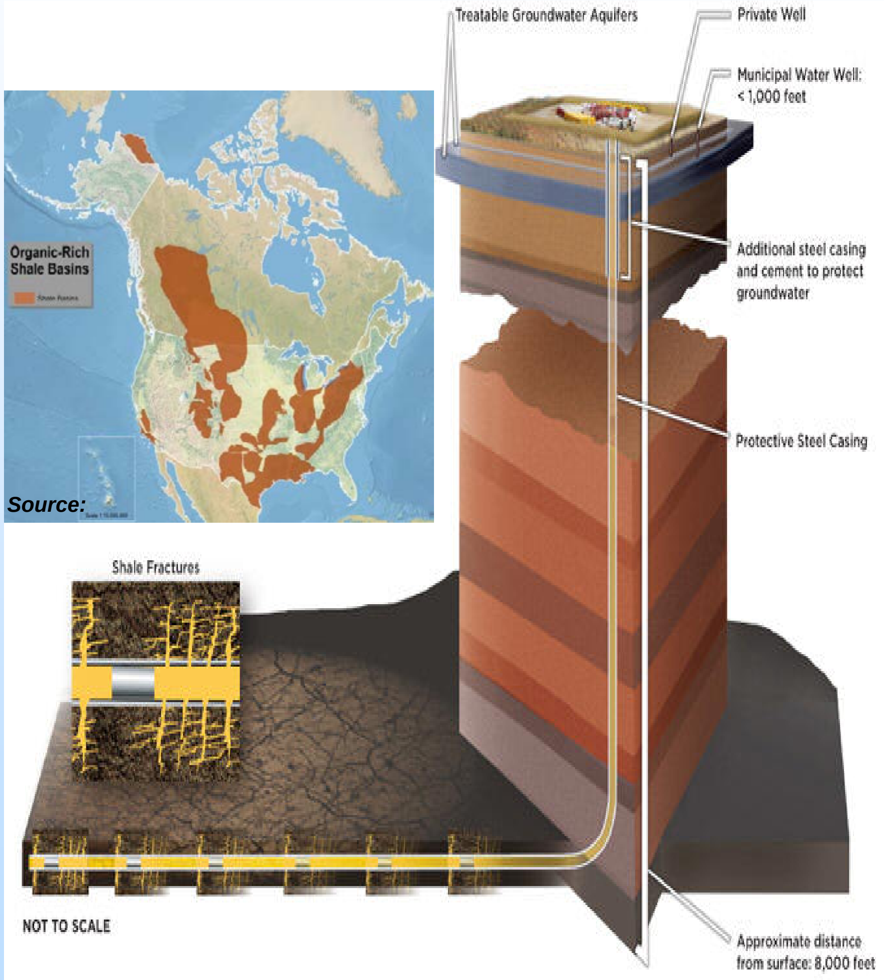
Technical Scope

Shales as Seals





Shales as Storage Reservoirs



Sources: HF illustration from National Energy Technology Laboratory (NETL), 2011), *Micro CT images by Rebecca Rodriguez, ORISE; Shale image from Reference: Lacazette , A. and Engelder, T. (1992) Fluid-driven cyclic propagation of a joint in the Ithaca Siltstone, Appalachian Basin, New York: p. 297 - 323 in B. Evans and T.-F. Wong (editors): Fault Mechanics and Transport Properties of Rocks; a festschrift in honor of W. F. Brace: Academic Press, San Diego.; NETL Carbon Storage Atlas IV (2012)*

Benefit to the Program

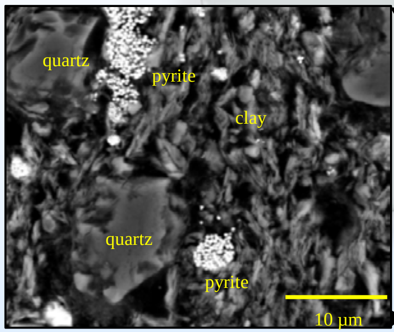
- Carbon Storage Program Goals Addressed:
  - Support industry's ability to predict CO_2 storage capacity in (*unconventional)* geologic formations to within ± 30 percent
  - Ensuring 99 percent storage permanence.
- Project Benefits:
  - Improve understanding of injection/storage performance of unconventional formations
  - Inform efficiency estimation for resource assessment
  - Insights feeding to seal characterization in integrated assessment of risk

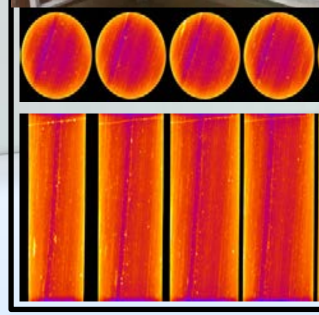
Project Overview:
Goals and Objectives

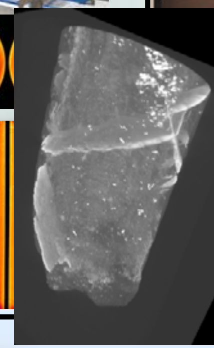
- Project Objectives
  - Evaluate matrix response to CO_2 exposure (sorption, swelling/shrinkage, geochemical interactions)
  - Characterize effective permeability and porosity of shale to CO_2
  - Experimental and simulation-based performance of CO_2 storage in/transport through shale with natural and engineered fractures
  - Reduced order characterization to improve resource estimation and quantitative risk assessment of geologic CO_2 storage

Science Base Feeding to Higher-Level Assessments

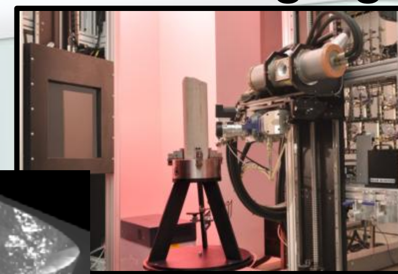
Micro-Scale Data Collection (CT, SEM, etc)



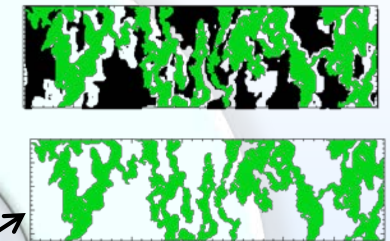




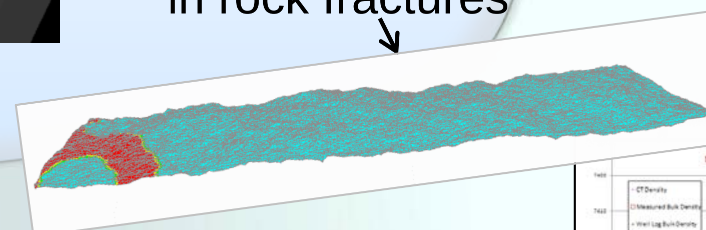
Core-Scale Flow and Imaging



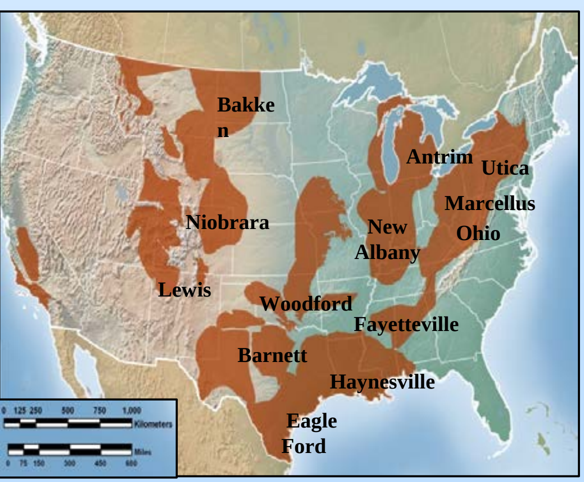
Data Conversion & Computational Fluid Dynamics



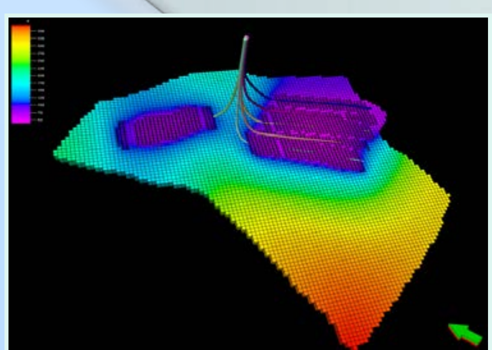
Gas/liquid flowing in rock fractures



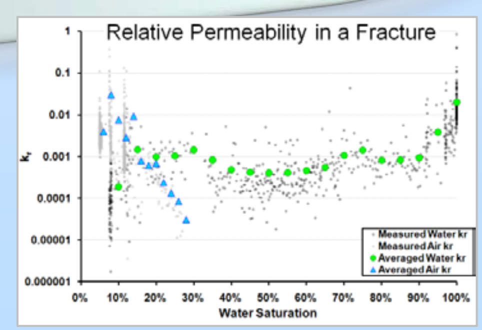
National-Scale Assessment

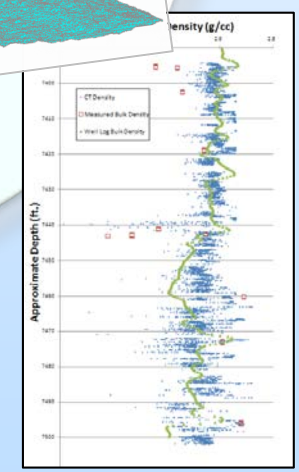


Well and Field-Scale Simulation



Multiscale Data Analysis

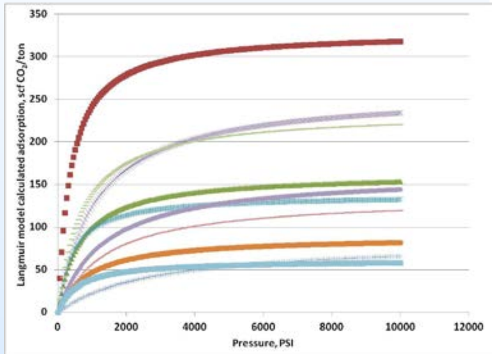




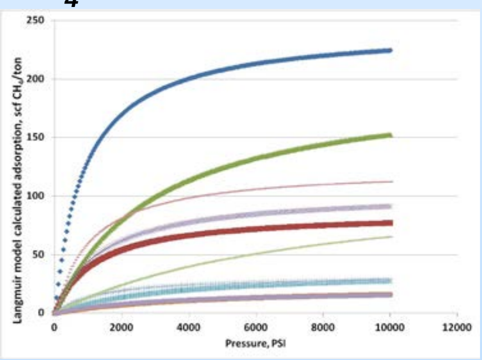
Comparison of Shale Density from CT Scans and Well Logs

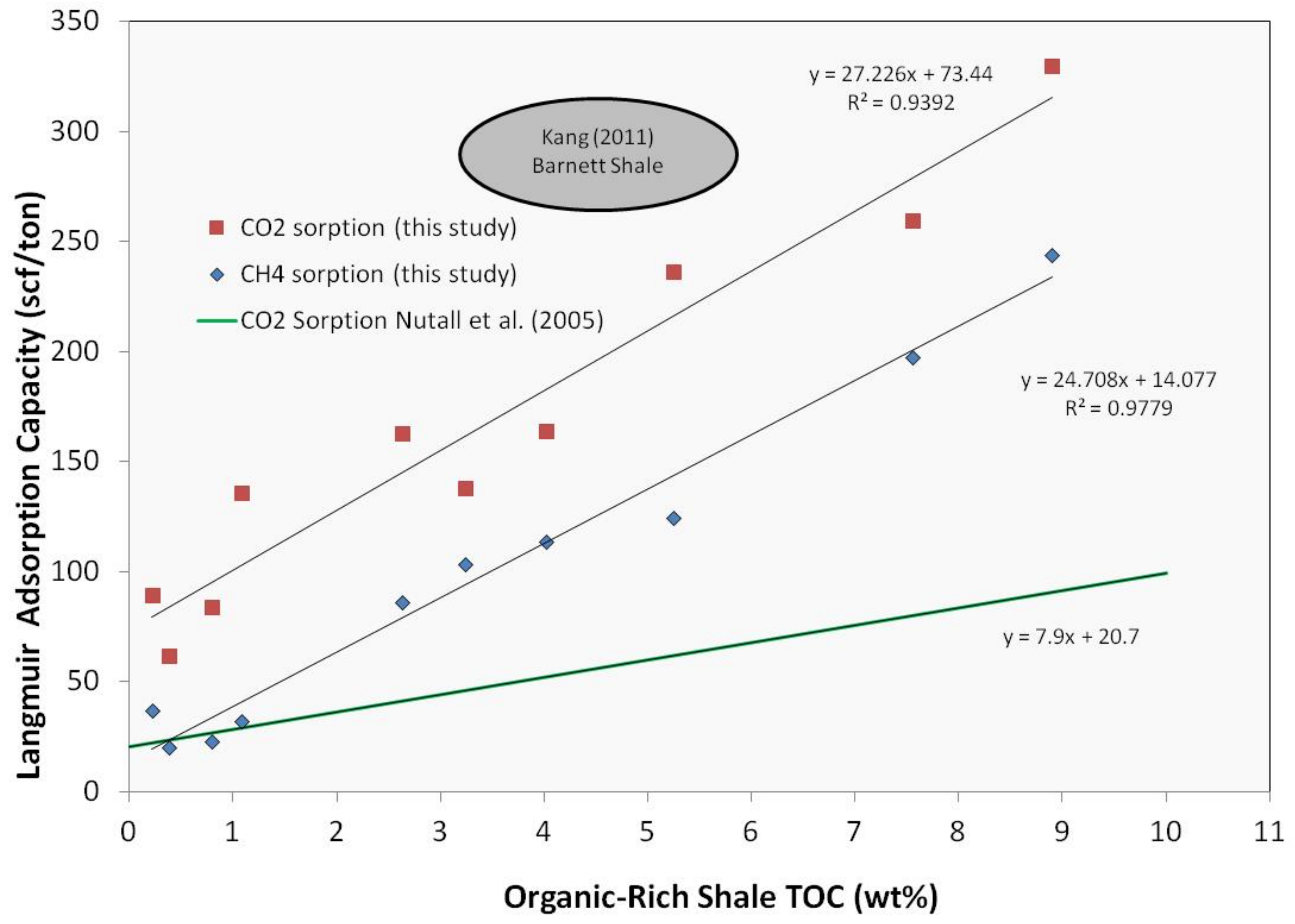
CO_2 and CH_4 Sorption capacity as function of %TOC (single-fluid isotherms)

CO_2 Isotherms



CH_4 Isotherms

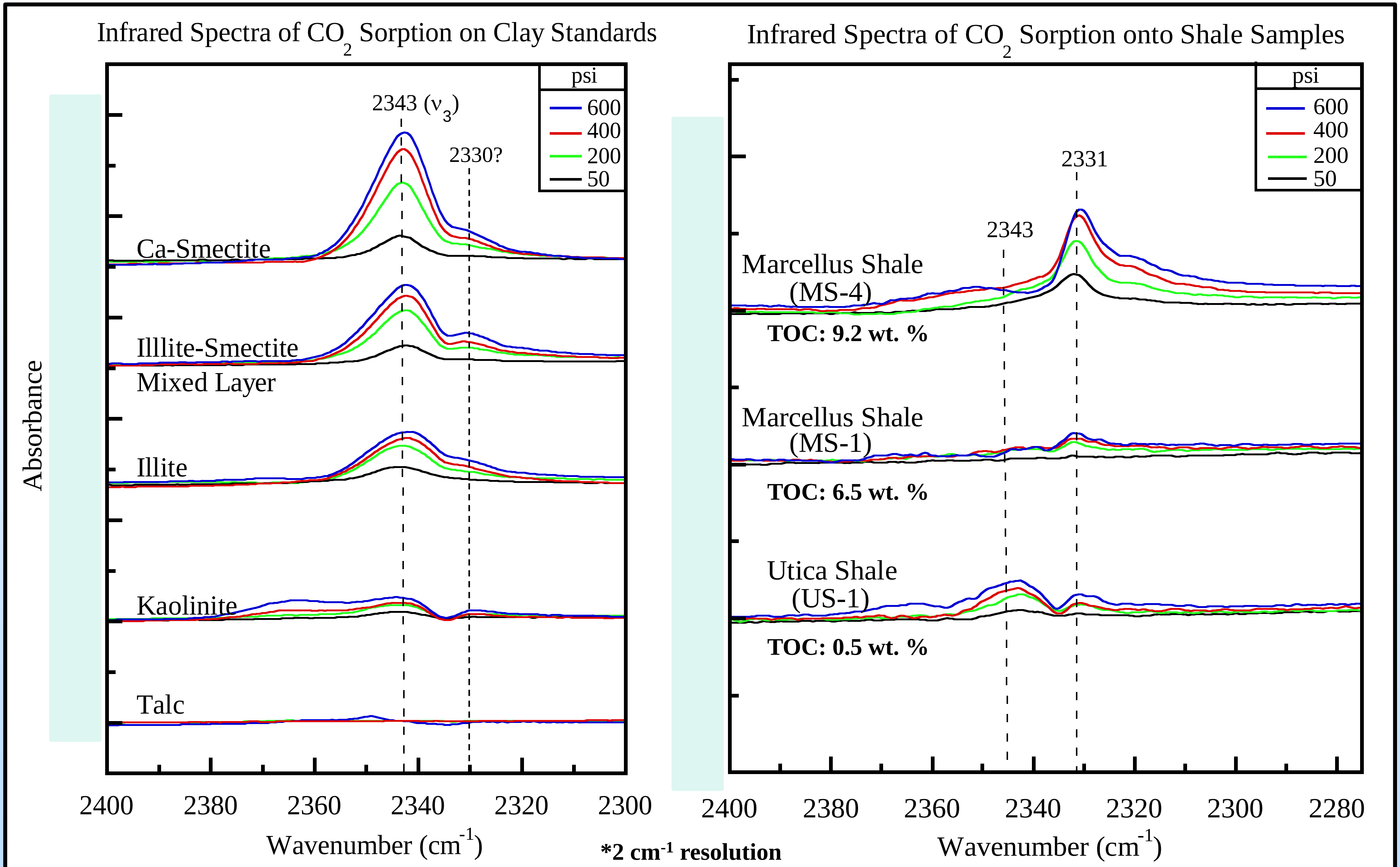




Nuttall, Brandon; Cortland F. Eble; James A. Drahovzal, and Mark Bustin, *Analysis of Devonian Black Shales for Potential Carbon Dioxide Sequestration and Enhanced Natural Gas Production*, Report DE-FC26-02NT41442 prepared by the Kentucky Geological Survey, University of Kentucky, for the U.S. Department of Energy, National Energy Technology Laboratory, December 30, 2005.

CO_2 Sorption Mechanisms: Fourier Transform-Infrared Spectroscopy (FT-IR)*

15 min CO_2 exposure at 40°C, 0-800 psi



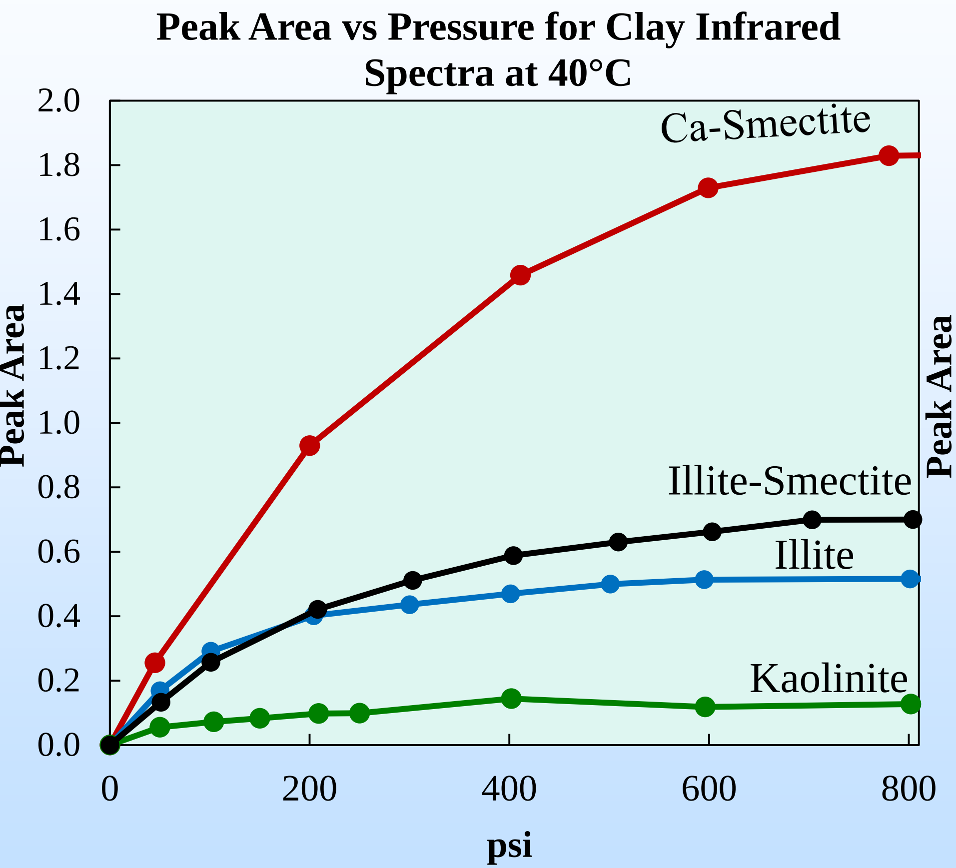
***2 cm^{-1} resolution**

Physically Sorbed CO_2 IR Peaks: 2350-2330 cm^{-1}

CO_2 Sorption on Shale Samples

FT-IR Data:

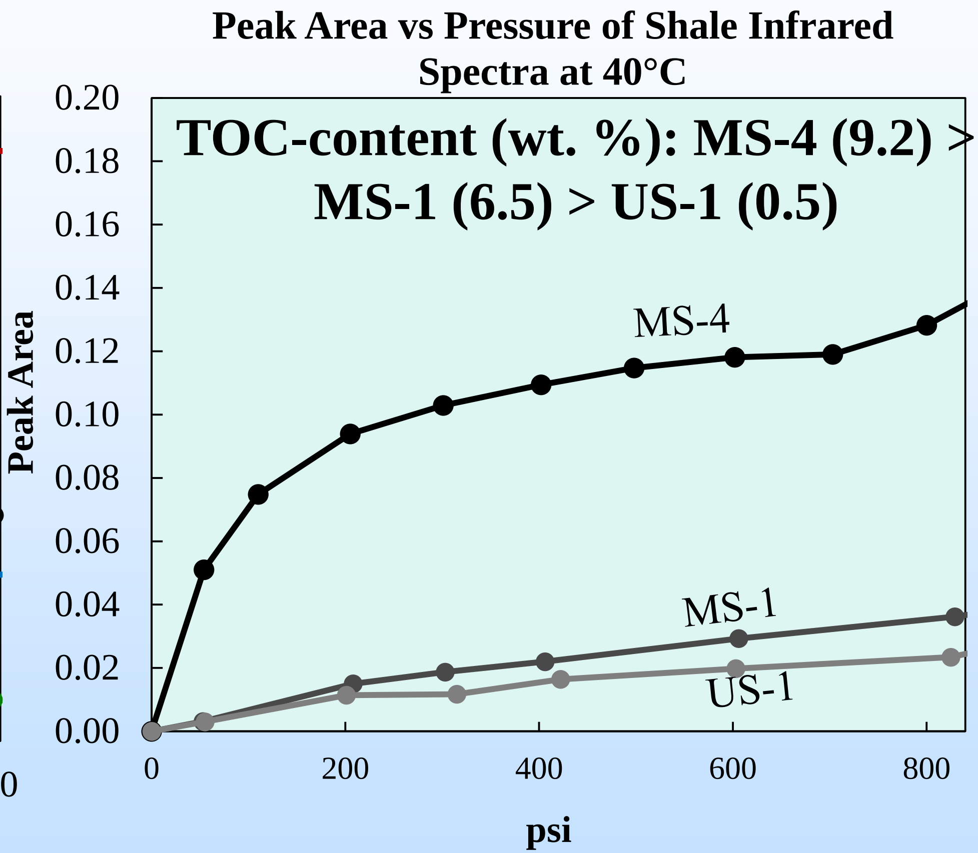
Area of 2343 cm^{-1} CO_2 Sorption Peaks



Integrated CO_2 peak area is not quantitative

FT-IR Data:

Area of 2331 cm^{-1} CO_2 Sorption Peaks*



*2343 cm^{-1} peak not strong enough to obtain reliable area measurements

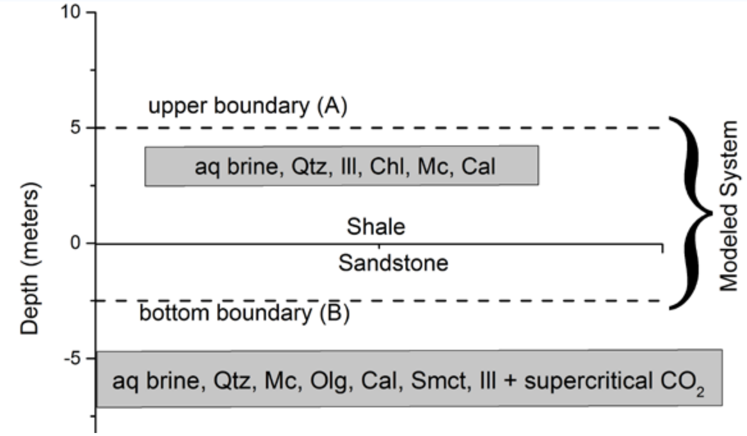
FT-IR trends compliment results of CO_2 isotherm measurements

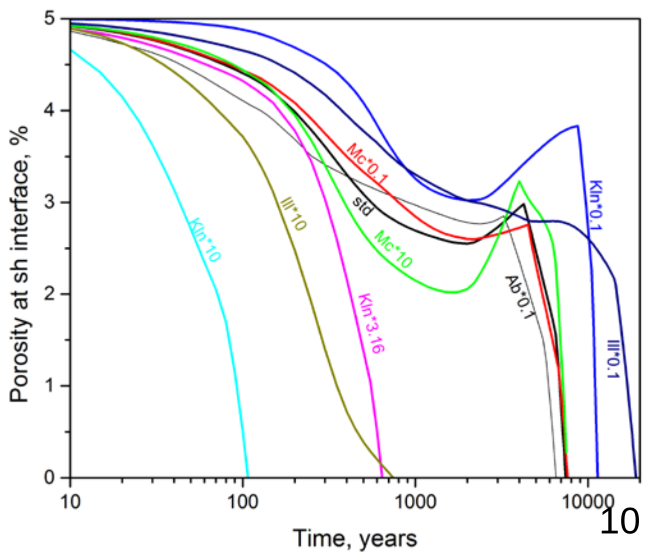
Geochemical Model Sensitivity and Caprock Interface

Study Problem: Geochemical calculations rely on uncertain thermodynamic & kinetic databases

Goal: *Characterize the mineral precipitation and dissolution processes that are important at brine/aquifer/caprock interfaces.*

Finding: *The precipitation and dissolution processes for minerals Chlorite, and carbonates Cc, Dol, Ank contribute to autosealing at the brine/aquifer/caprock interfaces.*

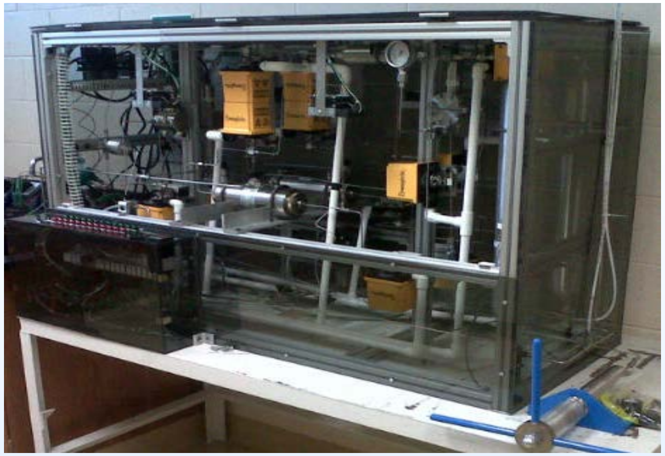




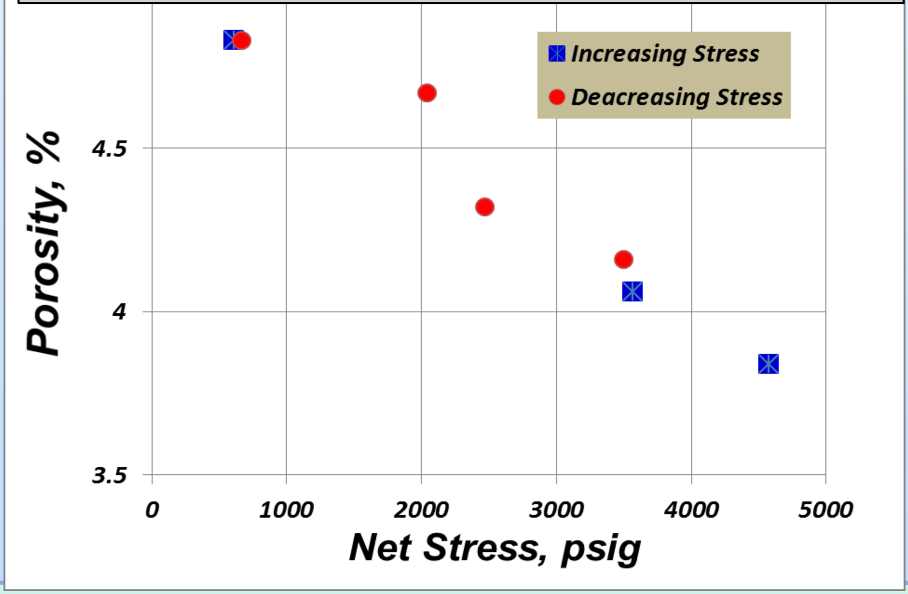
Source: Balashov, V. N. Brantley, S. L. Guthrie, G. D. Lopano, C. L Hakala, and J. A. Impact of geochemical kinetics at the reservoir/ shale interface on long term CO2 storage. Goldschmidt Conference June 8 – 13, 2014

Steady-State Permeameter

Capable of reproducing in-situ net stress, and measuring gas flow under partial liquid saturation



Effective porosity of shale as function of net stress



Effective permeability of shale as function of net stress

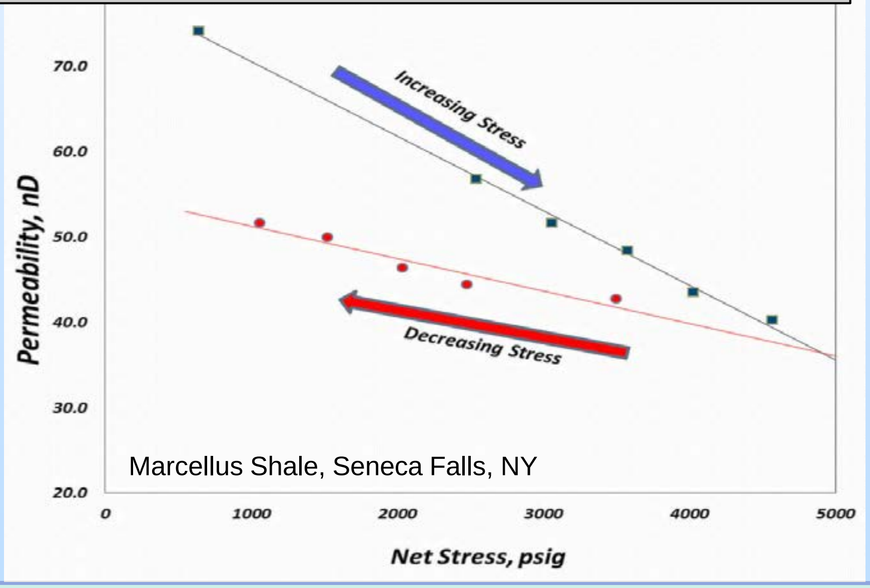
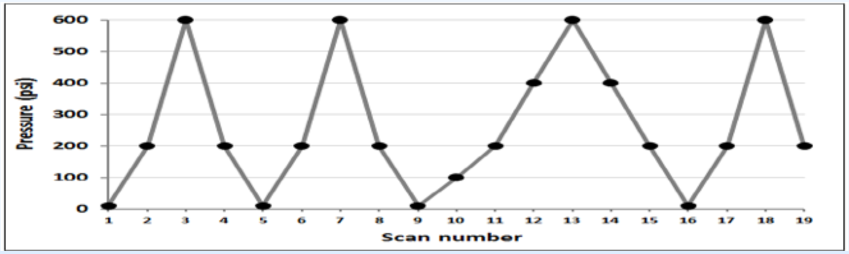


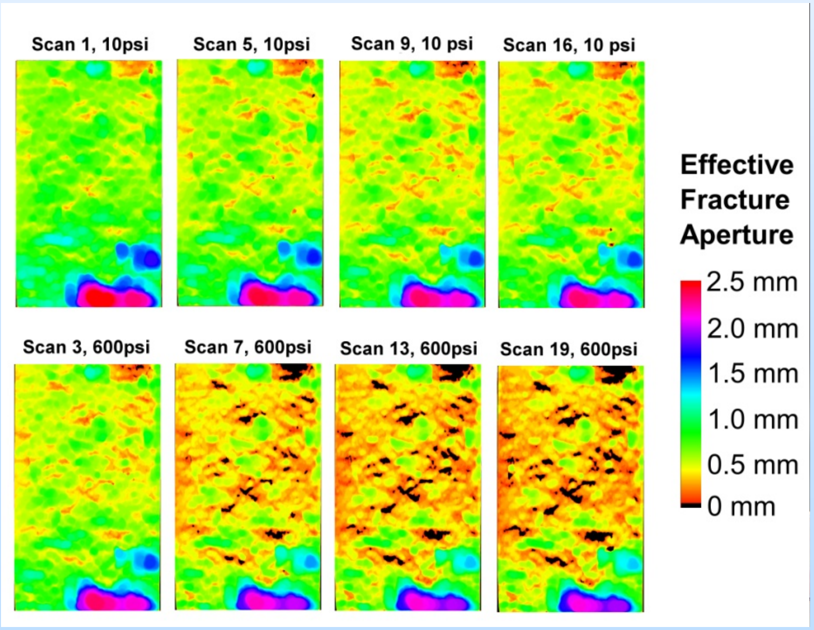
Image from: **Kashiar Aminian;** *Discussion of PPAL capability at: SPE/DOE 11765, Symposium on Low Permeability Gas Reservoirs, Denver, CO, March 13-16, 1983*
Soeder, D. J., 1988, Porosity and permeability of eastern Devonian gas shale: SPE Formation Evaluation, Vol. 3, No. 2, p. 116-124, DOI 10.2118/15213-PA.

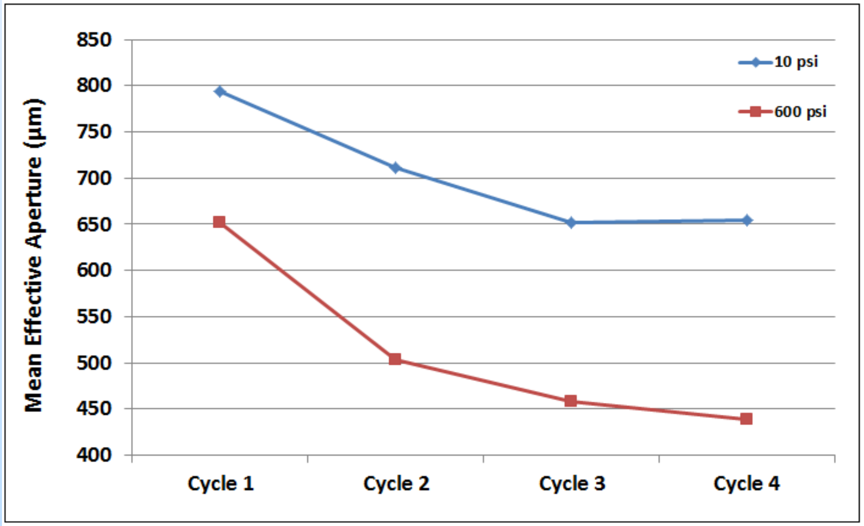
NETL

Coupling Mechanical Changes of Fractures to Hydraulic Changes

Cycling of confining pressure causes fracture asperities to break down, reducing effective fracture aperture



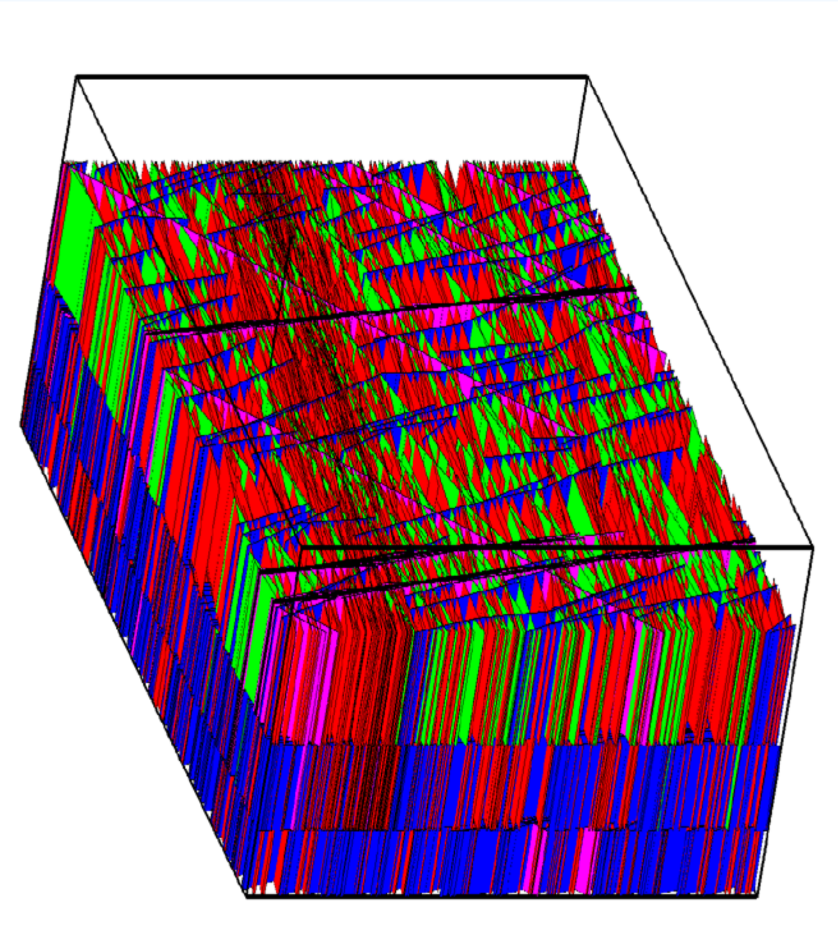




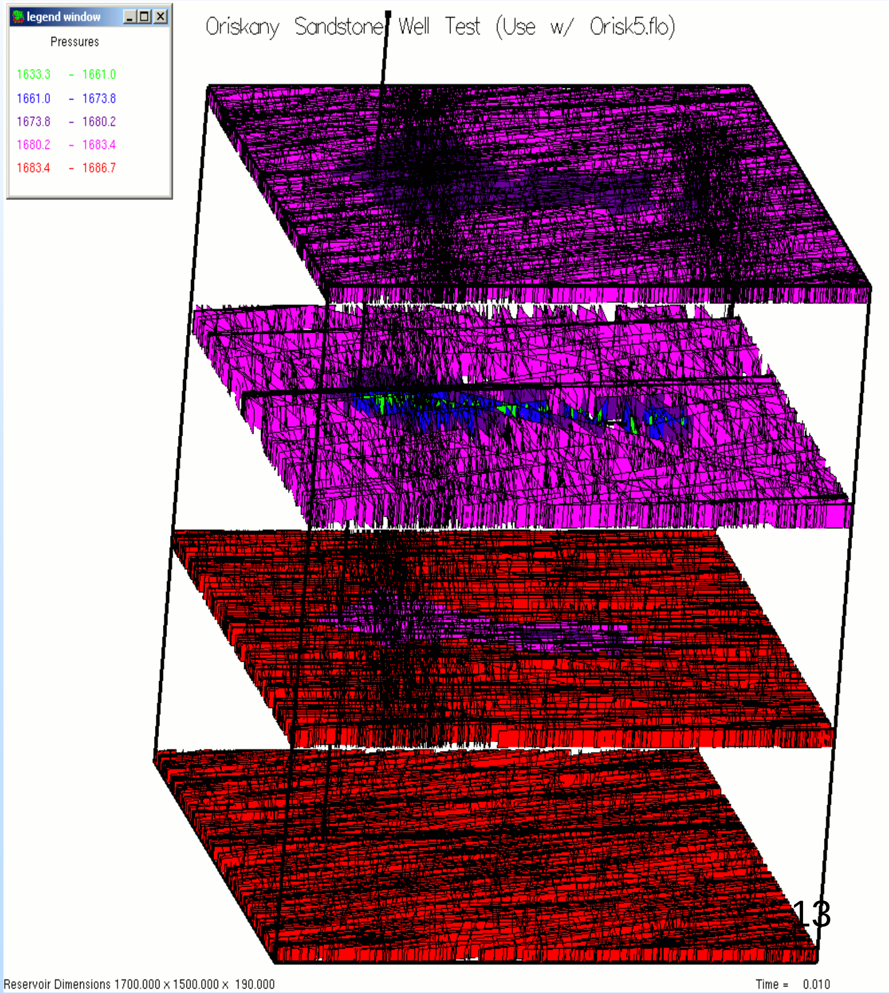
Source: Crandall, D. Gill, M., McIntyre, D.L., and Bromhal, G.S. (2013) ***Coupling Mechanical Changes of a Fracture to Hydraulic Changes***
SPE 165695-MS. prepared for SPE Eastern Regional Meeting held in Pittsburgh, Pennsylvania, USA, 20–22 August 2013. © 2013, SPE

Modeling CO_2 Flow in Fractured Geologic Media

FRACGEN stochastically generates fracture networks



NFFLOW models flow in discrete fracture networks



Images from: Sams, N. Overview of NFFLOW & FRACGEN. June 3, 2013

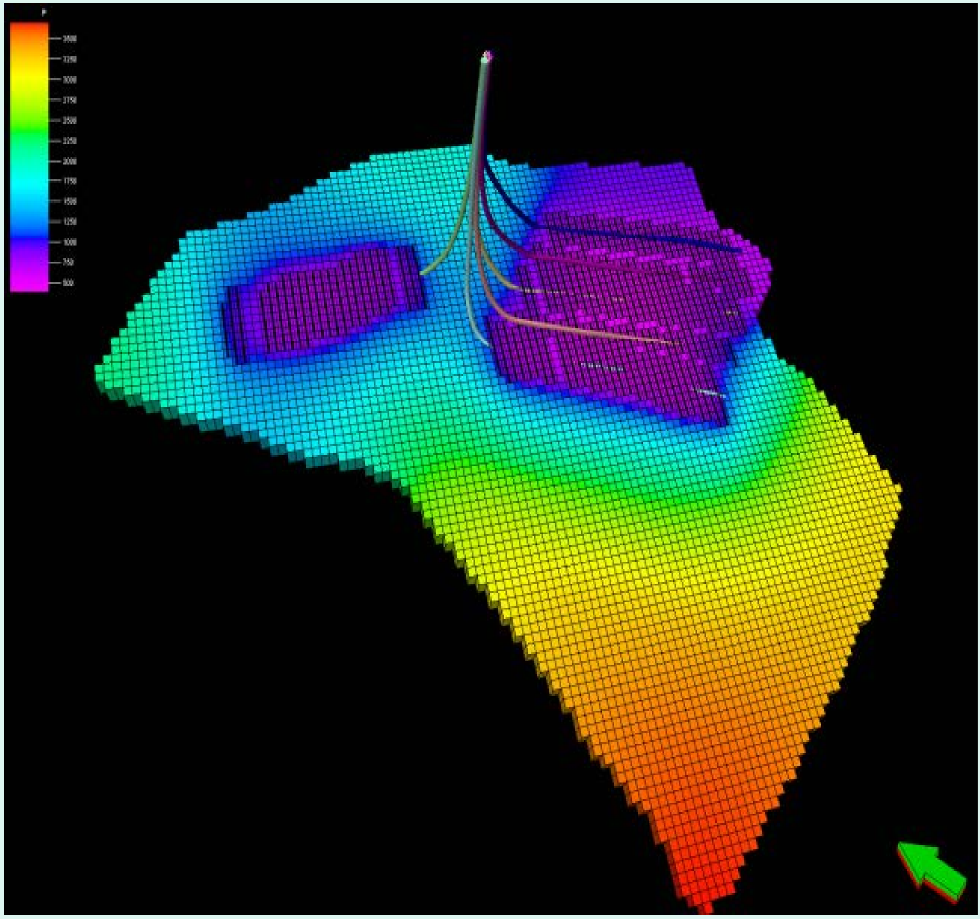
CO_2 Storage in Depleted Shale Gas Formations

Goal: *Develop a robust characterization of site-scale CO_2 storage and EGR potential of gas-bearing shale formations*

Scenario: Dry gas window, Marcellus, SW PA, Depth of 6,700 ft (~ 2,000 m), gross interval thickness of 120 ft (37 m), 145ºF (63ºC), Initial pressure 4,000 psi (27.6 MPa), matrix permeability 0.1 -1 (μD)

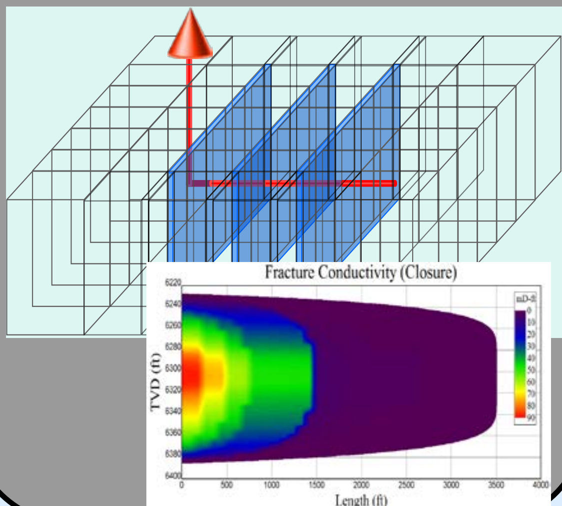
Sensitivity of CO_2 storage/EGR performance to:

- Fracture network characteristics
- Matrix CO_2 and CH_4 sorption characteristics
- Injector/producer distance
- Injection pressure
- Stress-dependent matrix perm.

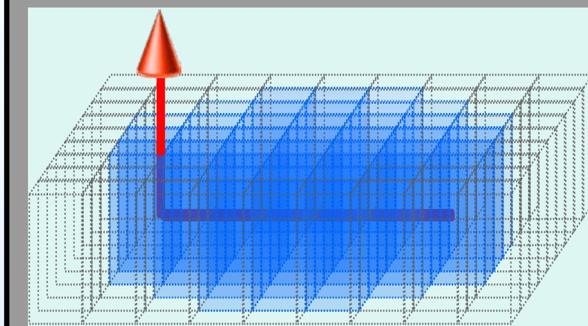


Representing Fracture Networks

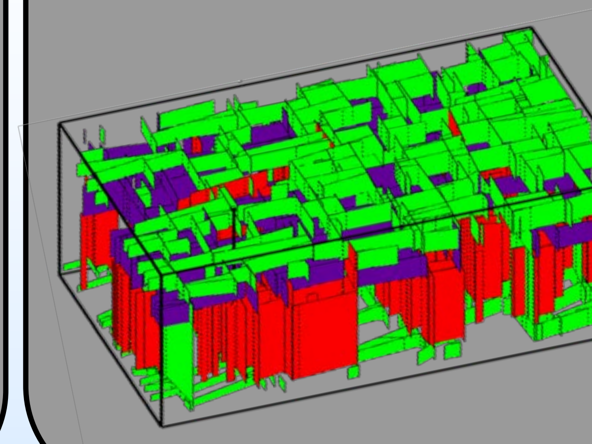
Discrete Transverse Fracture Planes



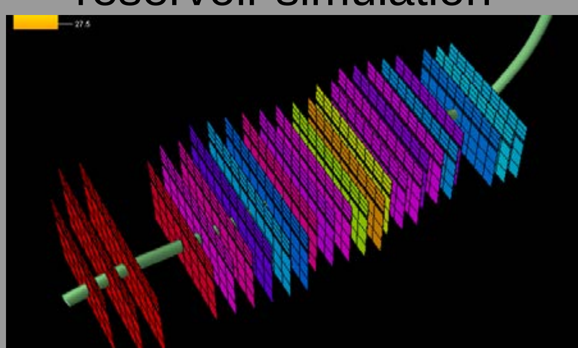
Crushed Zone Representation



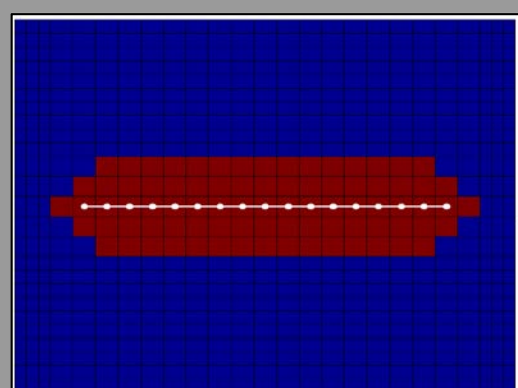
Semi-stochastic fracture Network



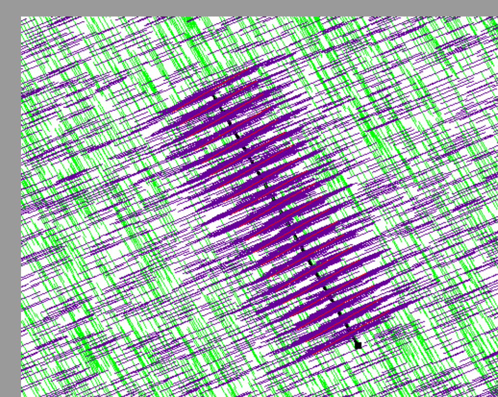
Discrete Fracture Modeling coupled with conventional reservoir simulation



Modified dual porosity, multiphase, compositional, multidimensional flow model



Semi-stochastic fracture network and flow modeling



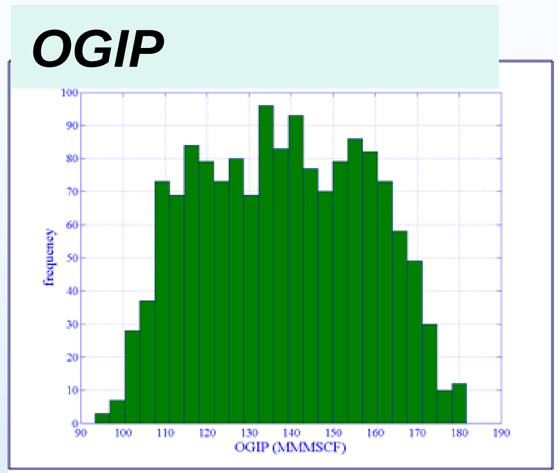
Single Lateral CO_2 Storage Scenario

Scenario: Constant pressure at 5000 psi, single lateral

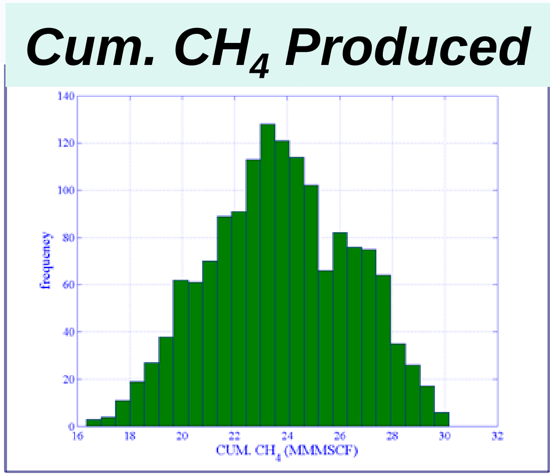
Uncertain Parameters:
h_{net}, Φ_{matrix}, $\Phi_{fracture}$, k_{matrix}, $k_{fracture}$, fracture spacing, Langmuir constants

MC with 1000 realizations

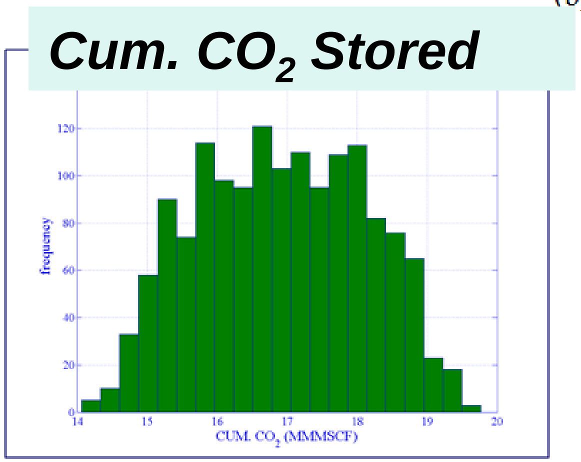
	P_{90}	P_{50}	P_{10}
OGIP (BSCF)	111	138	165
CH_4 Production over 30 Years (BSCF)	20.1	23.7	27.4
CO_2 Stored after 30 Years (BSCF)	15.3	16.9	18.5



(a)



(b)

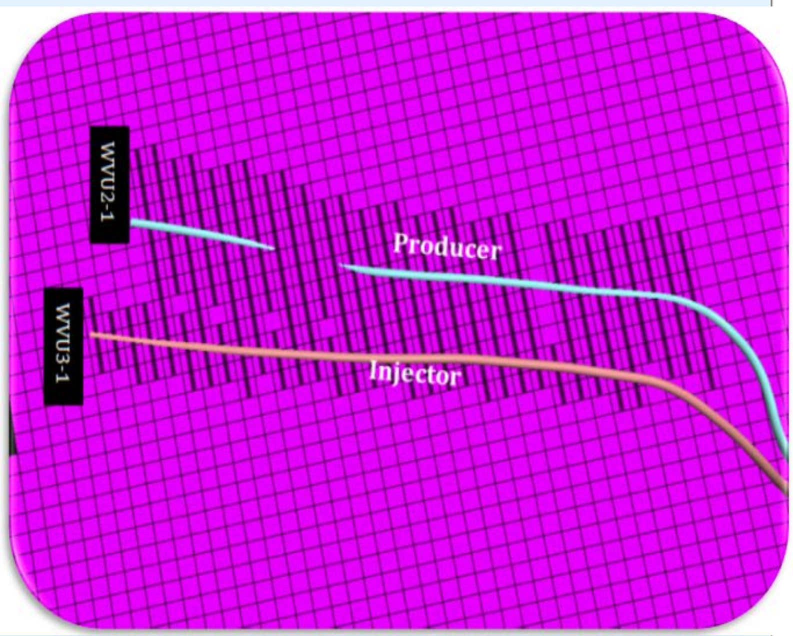


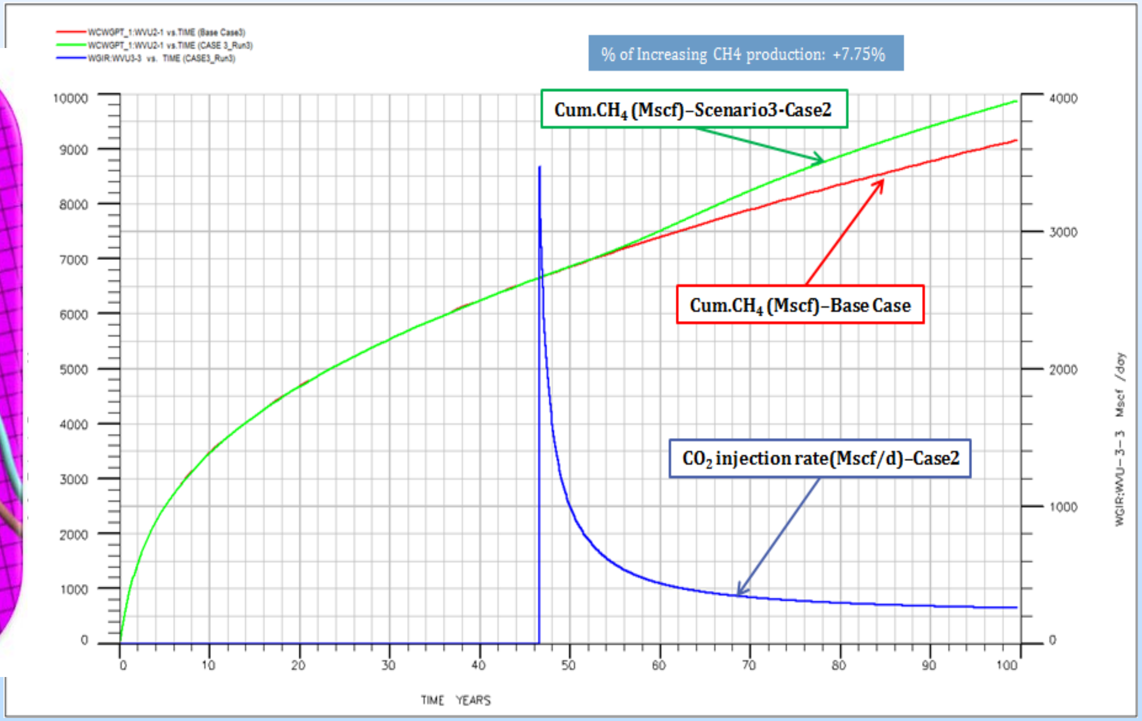
(c)

ICMI

CO_2 Storage and Enhanced Gas Recovery Scenario

- CO_2 Injection for EGR not expected to start until primary production complete (nominally 40 years)
- Models predict EGR recovery (technical) potential between 0 and 11% (above primary production)
- Time to breakthrough of 10% mole fraction in produced stream decreases significantly as SRV overlap of adjacent laterals increases

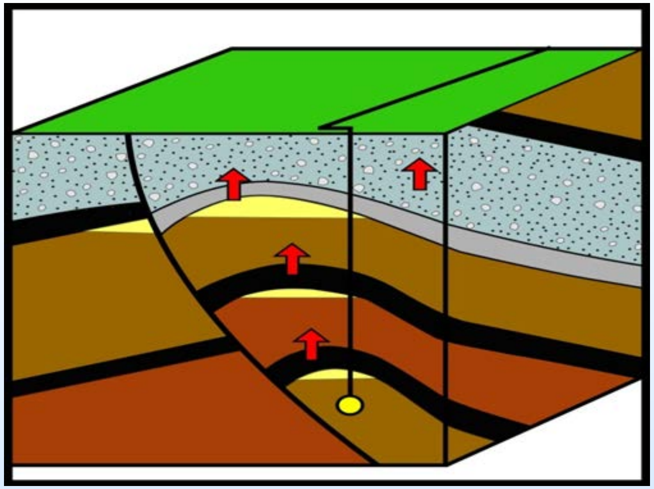


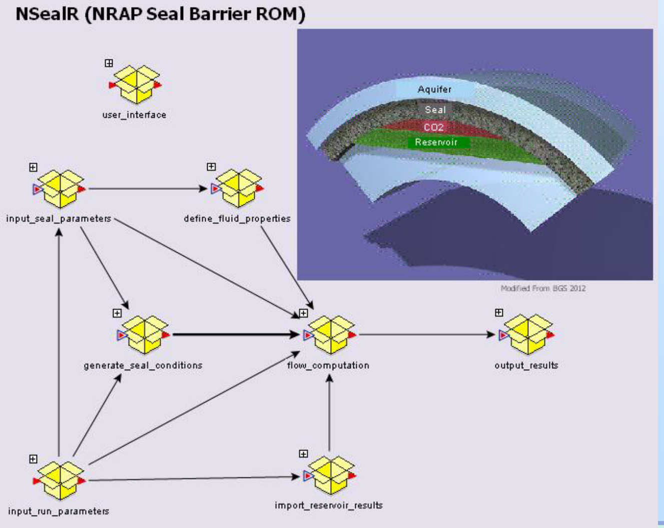


Sources: Kalantari-dahaghi, A, Mohaghegh, S. D. CO2-Driven Enhanced Gas Recovery and Storage in Depleted Shale Reservoir- A Numerical Simulation Study. *Manuscript #P317871, 2013* AICHE *Carbon Management Technology Conference.* Alexandria, Virginia, 21-23 October, 2013; Industrial Carbon Management Initiative (ICMI) Modeling Report

Flux through Fractured Seal ROM NSEALR

- Assumes thin, relatively impermeable, fractured rock unit, initially saturated with a saline water.
- Two-phase, relative permeability approach and 1-D Darcy flow of carbon dioxide through the horizon in the vertical direction
- User defined or stochastically varying permeability, porosity, seal thickness
- Correction for in situ stress on aperture values generated by the fractured rock model, including shear stress options





Accomplishments to Date

- Well/pad-scale characterization of CO_2 storage and EGR performance in depleted shale gas formations
- Preliminary experimental characterization of:
  - Shale sorption characteristics
  - Mechanisms of CO_2/shale interactions
  - Matrix permeability
  - Fracture flow
  - Pore imaging
- Reduced physics model characterizing flux through fractured seal
- Contributing to methodology for CO_2 storage in shale

Summary

– Future Plans

- Understanding shale pore type and structure
- Flow through nanopores on molecular scale
- Importance of pore effects at core-scale
- Matrix swelling/shrinkage effects
- Oil wet versus water wet (black shale vs. gray)
- Liquid and condensate reservoirs
- Simulation refinement and validation

Organization Chart

- NETL Office of Research & Development
  - Predictive Geosciences Division
  - Engineered Natural Systems Division
  - Material Characterization Division
- URS Corp.
- West Virginia University, Penn State University, Carnegie Mellon University

Gantt Chart

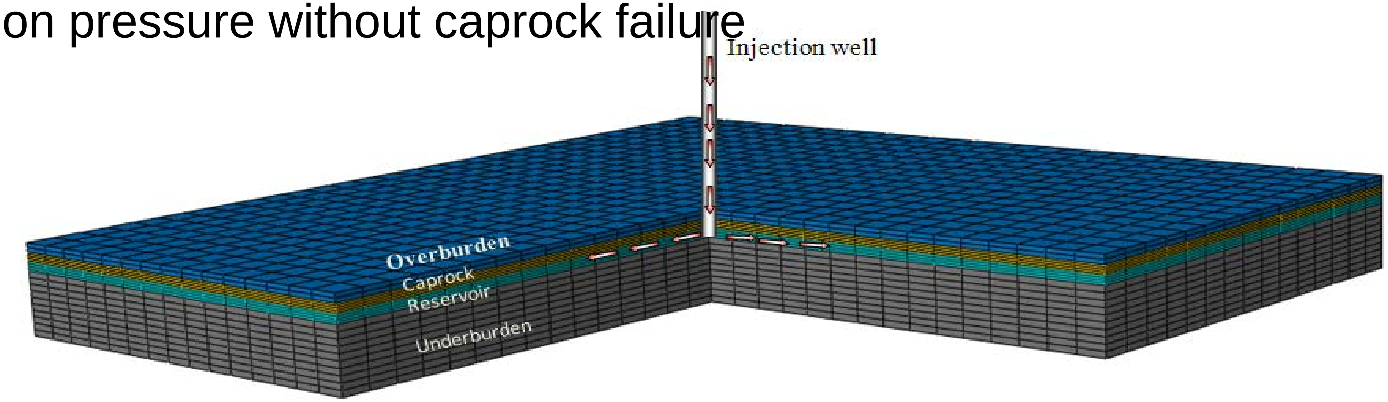
Carbon Storage
FWP Number Car Stor_FY14
Schedule and Milestones

Task No.	Activity Name (Task/Sub-task)	Start	Finish	FY14 (Q1–Q4)
1.0	**Project Management**	**10/1/13**	**9/30/14**	
1.1	Project Management	10/1/13	9/30/14	
2.0	**Reservoir and Seal Performance**	**10/1/13**	**9/30/14**	M1.14.2.A
2.1	Impact of CO_2-Brine-Rock Chemistry on Storage Formations and Seals	10/1/13	9/30/14	
2.2	Impact of Microbial Processes on Storage Formations and Seals	10/1/13	9/30/14	
2.3	Impact of CO_2 on Shale Formations as Seals	10/1/13	9/30/14	
2.4	Characterization of Reservoir and Seal Material Performance	10/1/13	9/30/14	
2.5	Understanding of Multiphase Flow for Improved Injectivity and Trapping	10/1/13	9/30/14	
2.6	Geochemical Model Sensitivity at Caprock Interfaces	10/1/13	9/30/14	
3.0	**Monitoring Groundwater Impacts**	**10/1/13**	**9/30/14**	M1.14.3.A
3.1	Natural Geochemical Signals for Monitoring Groundwater Impacts	10/1/13	9/30/14	
4.0	**Resource Assessments and Geospatial Resource**	**10/1/13**	**9/30/14**	M1.14.4.A
4.1	Resource Assessments	10/1/13	9/30/14	
4.2	Geospatial Data Management	10/1/13	9/30/14	
5.0	**Monitoring CO_2 and Pressure Plume**	**10/1/13**	**9/30/14**	M1.14.5.A
5.1	Development of Technology to Monitor CO_2 and Pressure Plume	10/1/13	9/30/14	
6.0	**Catalytic Conversion of CO_2 to Industrial Chemicals**	**10/1/13**	**9/30/14**	M1.14.6.A
6.1	Catalytic Conversion of CO_2 to Industrial Chemicals	10/1/13	9/30/14	

Milestone   Summary   Page 1 of 1

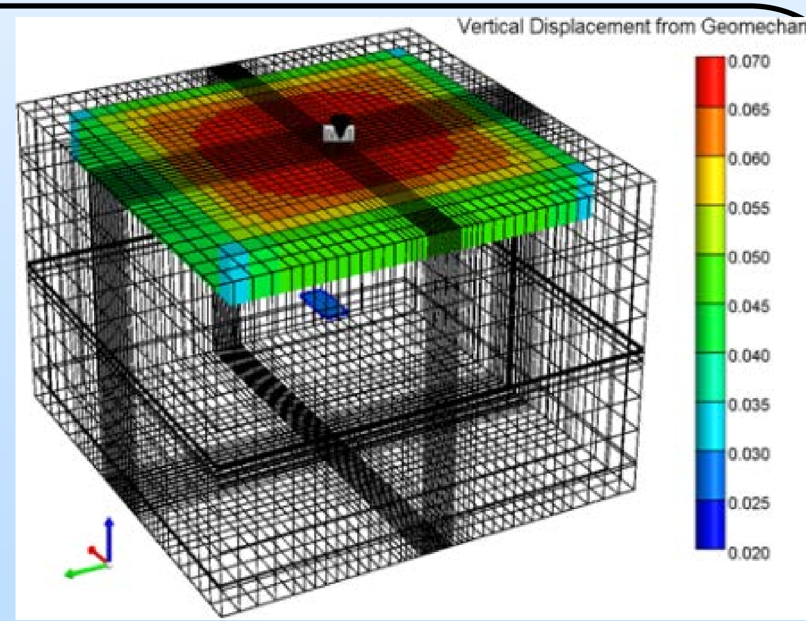
Coupled Fluid Flow and Geomechanical Modelling

3-D, single phase Finite Element Model to estimate maximum allowable injection pressure without caprock failure



Ground Deformation

- Maximum computed surface displacements are about 0.07 ft (21.3 mm).
- Can monitor with tiltmeter array



Vertical displacements above injection zone

Related Studies

- Nuttall et al., (2005) – Kentucky Geologic Survey
  - KGS developed the first volumetric estimates of CO_2 storage potential in the Carbonaceous (black) Devonian gas shales that underlie Kentucky, estimating that as much as 28 Gt could be stored there.
- Advanced Resources International (2013)
  - Basin-level assessment of CO2 and EGR potential, reservoir simulation, novel monitoring, techno-economic assessment
- Tao & Clarens (2013) (U. Virginia)
  - Estimating CO_2 storage in Marcellus shale
- Zobak et al. (Stanford)
  - evaluate physical and chemical interactions between CO_2 and shale, imaging of fluid migration in shale
- Ripepi et al. (Virginia Tech)
  - Simulation and field demonstration in Central Appalachia

References: Tao, Zhiyan and Clarens, Andres. Estimating the Carbon Sequestration Capacity of Shale Formations Using Methane Production Rates. Environmantal Science & Technology 2013, 47, 11318 – 11325. Advanced Resources International, Inc. Assessment of Factors Influencing Effective CO2 Storage Capacity and Injectivity in Eastern Gas Shales.;Final Technical Report. DE-FE0004633 October 23, 2013

(2) Experimental Analysis of CO_2 Storage in Organic-rich Shale

Purpose:

Examine & quantify CO_2 sorption capacity of *individual* clay standards & shale samples

Determine relative roles of kerogen, clay, & clay type in CO_2 storage potential of shales

Analytical work conducted on shale samples and clay standards

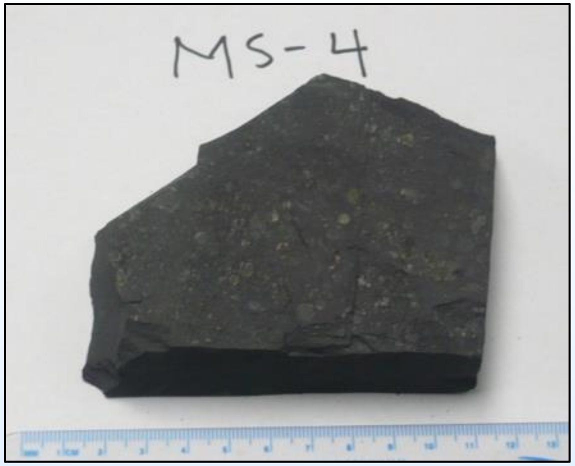
Sample	Description	He Pycnometry	E-SEM	FT-IR (std)	FT-IR (T&P)	CO_2 Adsorption Isotherms	TOC	XRD
Shale Samples								
MS-1	Marcellus: *Oatka Creek*	Y	Y	Y	Y	Y	Y	Y
MS-4	Marcellus: *Union Springs*	Y	Y	Y	Y	Y	Y	Y
US-1	Utica: *Flat Creek*	Y	Y	Y	Y	Y	Y	Y
Clay Standards*								
STx-1	Ca-Smectite	Y	-	Y	Y	Y	-	-
IMt-2	Illite	Y	-	Y	Y	Y	-	-
KGa-1b	Kaolinite	Y	-	Y	Y	Y	-	-
ISCz-1	Illite-Smectite	Y	-	Y	Y	Y	-	-
Talc	control	-	-	Y	Y	-	-	-

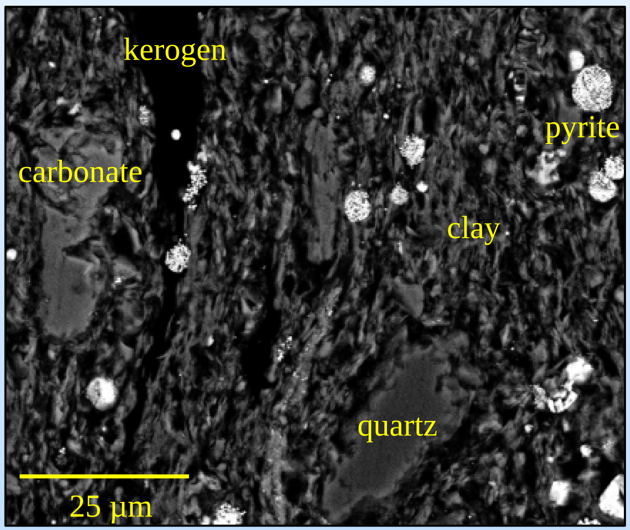
*All clays are natural standards obtained from the Clay Mineral Society

“Y” indicates the procedure has been conducted on the sample

Organic-rich Shale Outcrop Samples

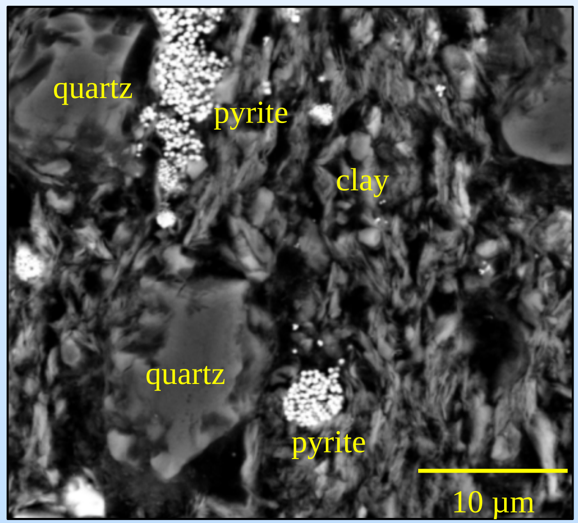
Marcellus - *Union Springs*





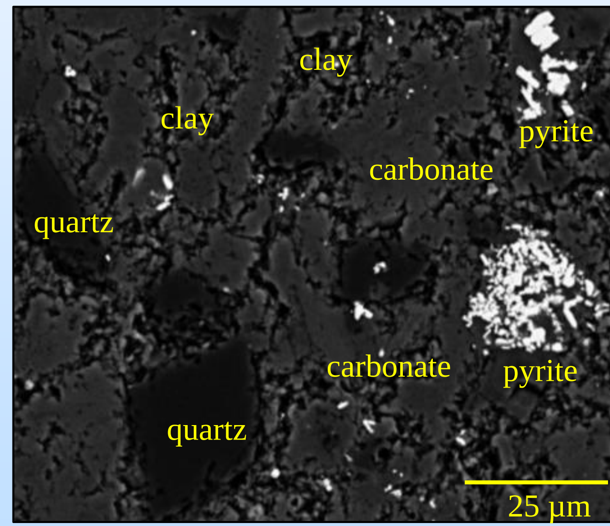
TOC = 9.20 wt. % (σ 0.60)

Marcellus - *Oatka Creek*



TOC = 6.51 wt. % (σ 0.22)

Utica - *Flat Creek*



TOC = 0.45 wt. % (σ 0.17)

Quartz + Clay (e.g. illite, chlorite, kaolinite) + Carbonate + Pyrite + Kerogen ± Feldspar

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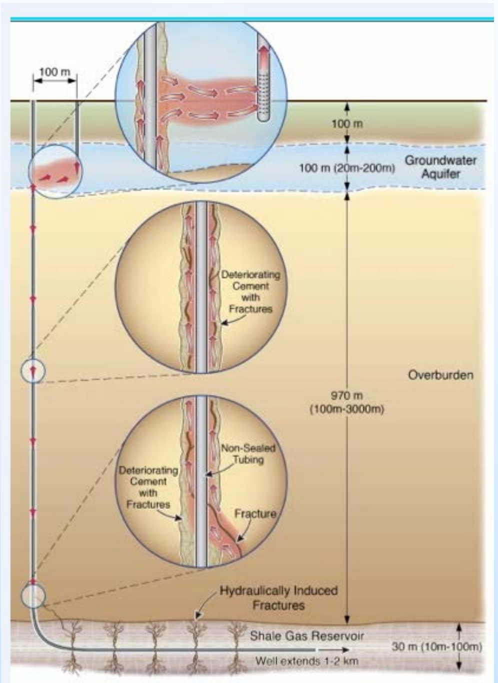
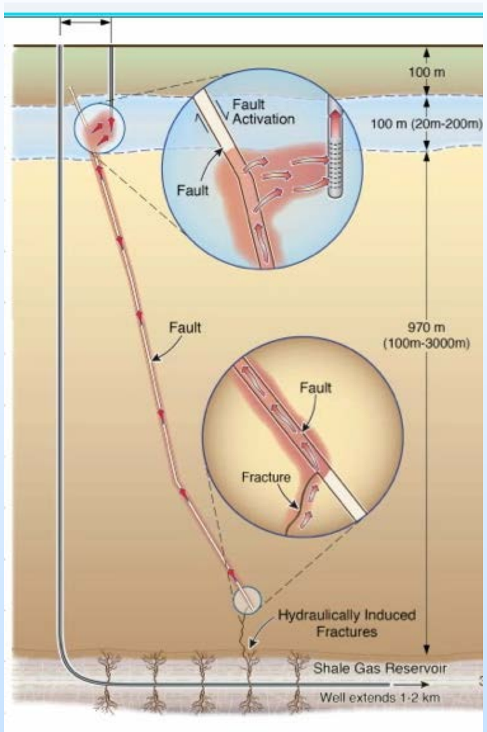
Key Findings: CO_2 Storage in Shale

- Without HF and natural gas production, CO_2 can not be injected
- Storage predominantly as free-phase CO_2 in fractures – low permeability matrix limits amount of matrix available for sorption
- Favorable assumptions about Langmuir characteristics results in only a small increase in storage (sorbed phase)
- Storage ~ 50,000 tonnes per fractured stage
- CO2 storage is not much greater in injector/producer scenario, and can be less in cases with significantly overlapping SRV

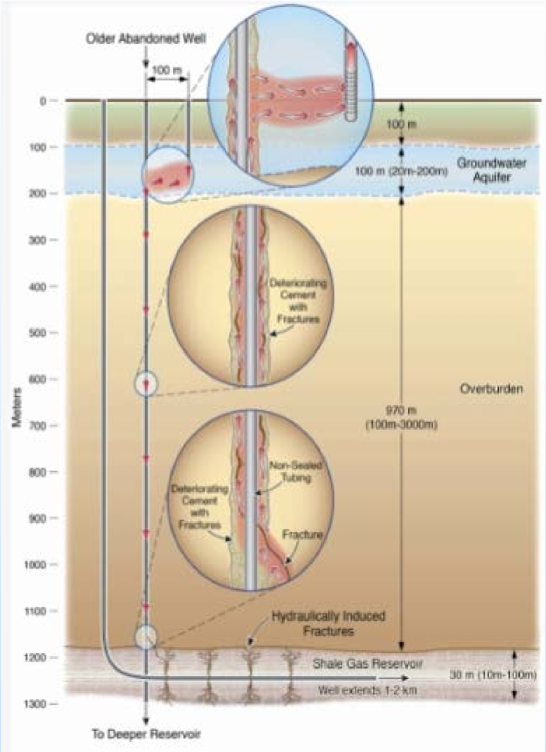
Potential Fluid Leakage Pathways from Unconventional HC Formations (US EPA, 2012)



Leakage through the annuli of the vertical drilling well

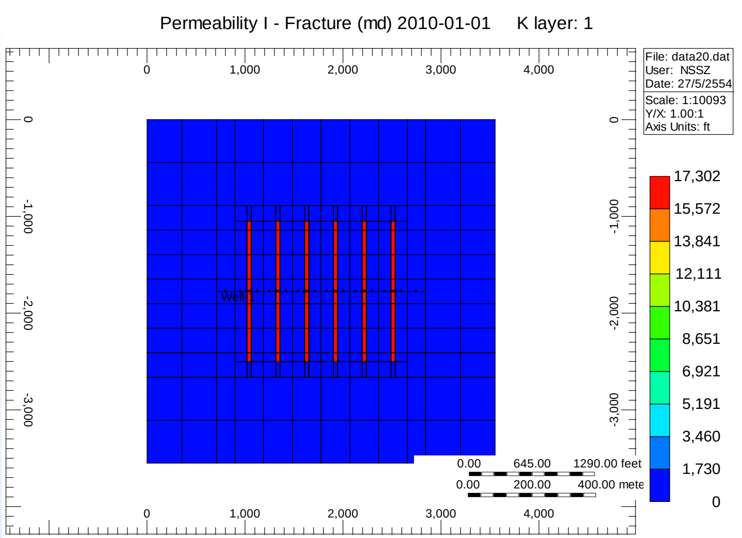


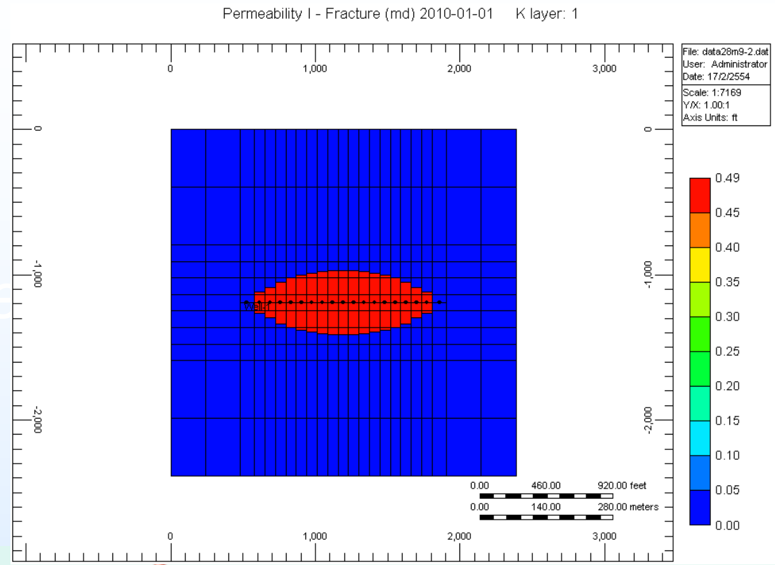
Leakage through a natural fault

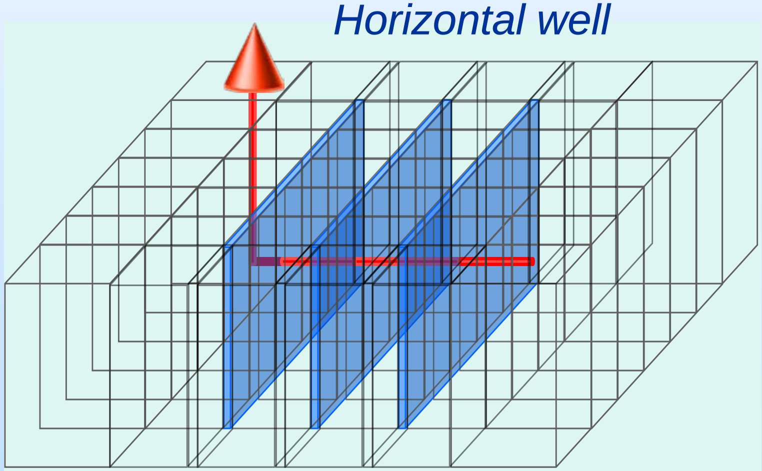


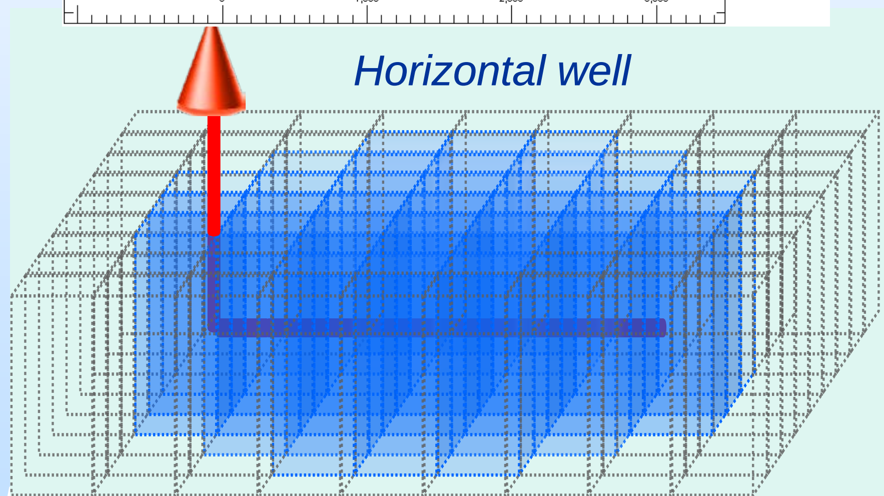
Leakage through an abandoned well

Representation of Horizontal Wells with Transvers Hydraulic Fractures
Evaluating the potential viability of an Equivalency Network









Discrete transverse fracture representation

?=

Crushed zone representation

Content Contributed by: *Turgay Ertekin, Penn State University Department of Energy and Mineral Engineering*

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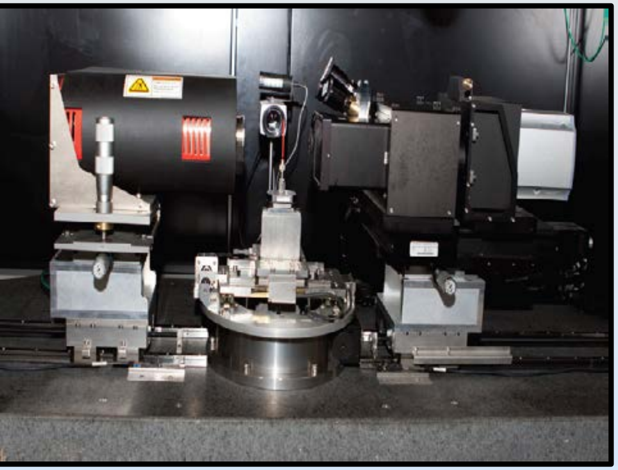
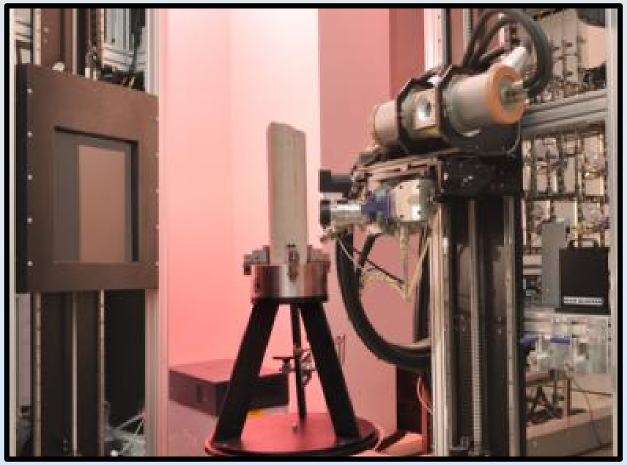
NETL ORD Multi-Scale CT Flow and Imaging Facilities





Micro CT Scanner
- Resolution 10^{-6} to 10^{-5} m
- Pore scale

Industrial CT Scanner
- 10^{-6} to 10^{-3} m
- Pore & core scale
- Pressure & flow controls

Medical CT Scanner
- 10^{-4} to 10^{-2} m
- Core scale
- P, T, and flow controls

Precision Petrophysical Analysis Laboratory

Effective porosity and permeability of shale to CO_2/CH_4 over range of effective stress, and characterization of hysteresis effects

- *Steady-state flow measurement, research quality data*
- *Capable of running different gases under different pressures, including nitrogen, methane and carbon dioxide.*
- *Capable of reproducing in-situ net stress, and measuring gas flow under partial liquid saturation.*
- *Can also measure pore volume to gas, adsorption isotherms and PV compressibility using N_2, CH_4 or CO_2*
- *Uses stable gas pressure as a reference for flow measurement*
    - *Temperature controlled*
    - *Stable to one part in 500,000*
    - *Target flow measurement is 10^{-6} standard cm^3 per second*

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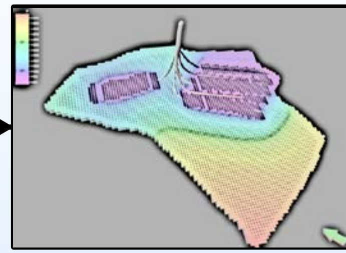
Image from: Kashiar Aminian; *Discussion of PPAL capability at: SPE/DOE 11765, Symposium on Low Permeability Gas Reservoirs, Denver, CO, March 13-16, 1983*

West Virginia University
Petroleum & Natural Gas Engineering

Linked SRM-Economic Screening Tool Modeling Approach

Field Properties
- Site location/properties
- Well/Completion details
- TOC

Flood Scenario Definition
- Configuration of well pad (# laterals/adjacency)
- Injection Schedule



Scenario Technical Performance
CO_2 injectivity over time, bottomhole pressure over time, produced gas rate/composition over time

Calculate Mass of CO_2 stored through flood

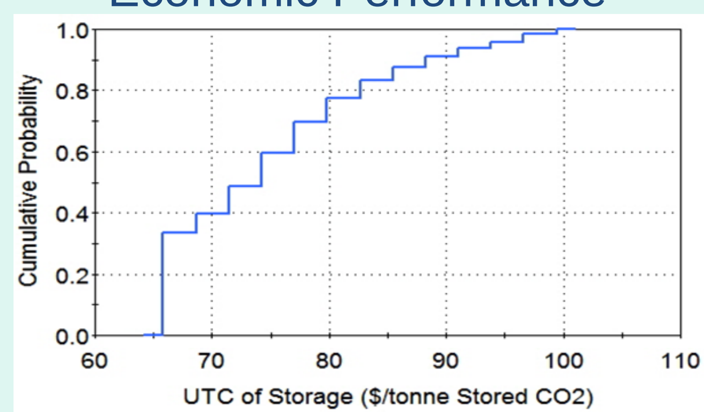
Dynamic link library

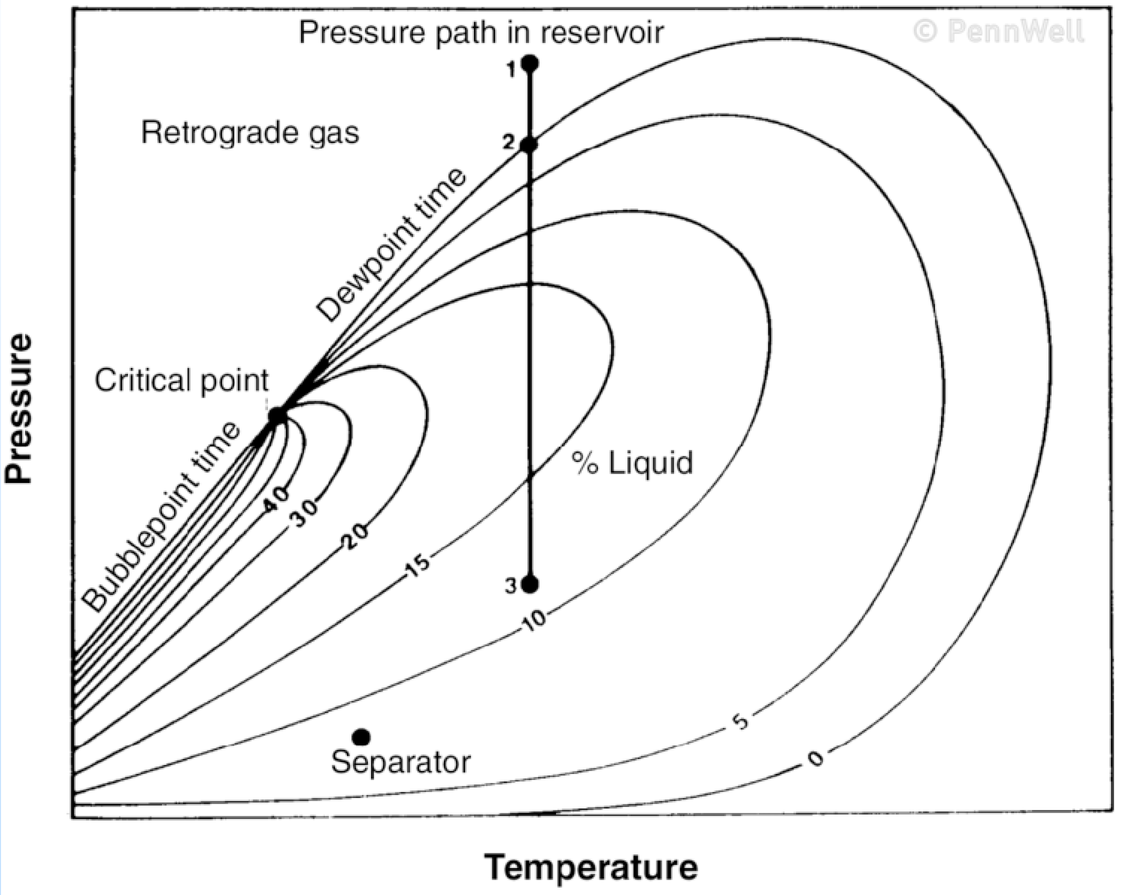
Financial Parameters
- CO_2 storage / NG value
- Electricity cost
- Interest rate
- Debt/equity ratio

Operational Parameters
- Source/sink distance
- Pipeline pressure
- Workover frequency

Economic Screening Model

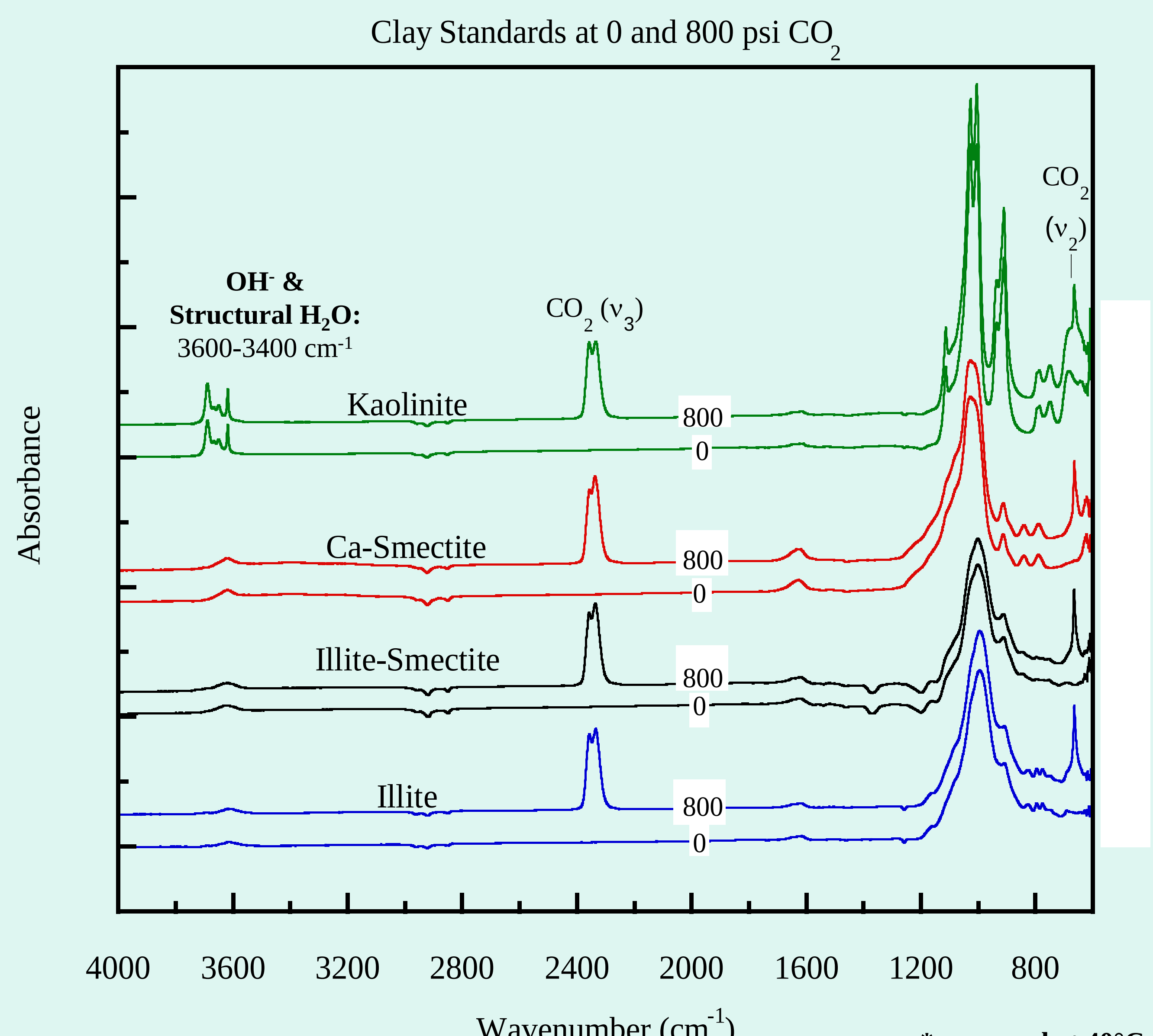
Scenario Economic Performance





Source: ***The Properties of Petroleum Fluids*****, second edition, by William D. McCain Jr. Copyright Pennwell Books, 1990**

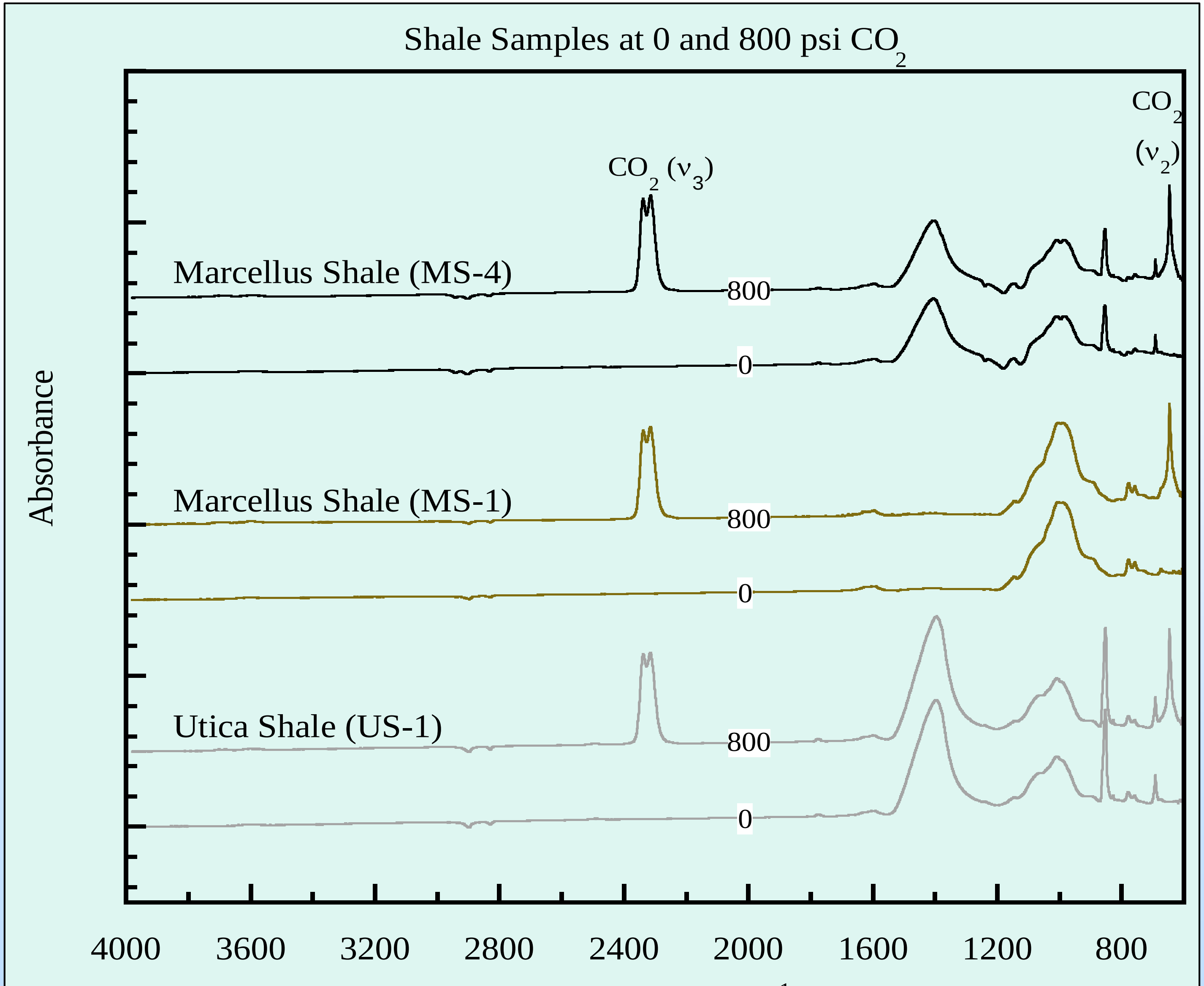
CO_2–Clay Interactions: FT-IR Spectroscopy*:



***measured at 40°C**

Chemically Sorbed CO_2 IR Peaks: 1400, 830, 720 cm^{-1}

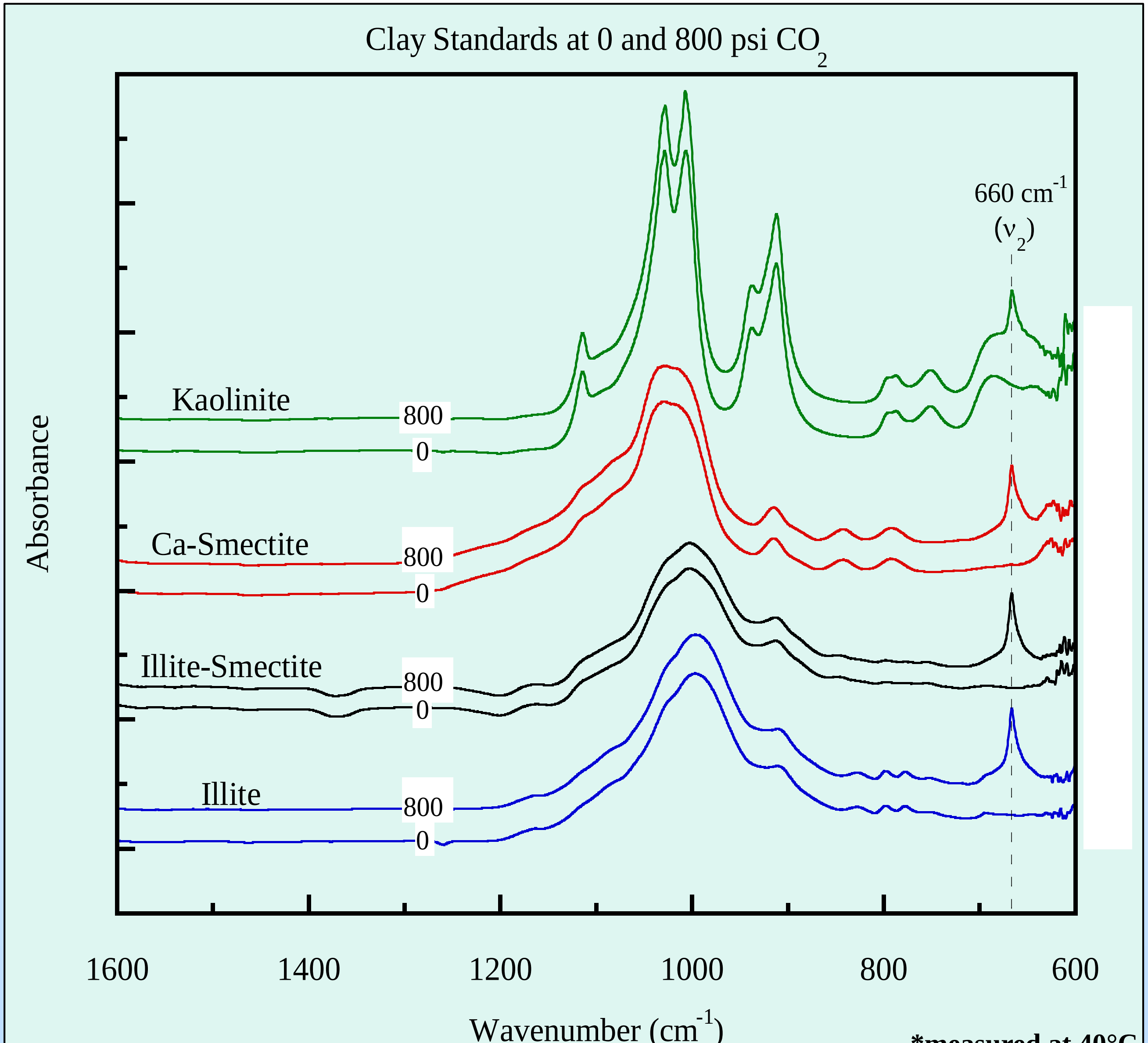
CO_2–Shale Interactions: FT-IR Spectroscopy*:



***measured at 40°C**

No changes observed in IR spectra with addition of CO_2 and pressure

CO_2–Clay Interactions: FT-IR Spectroscopy*:



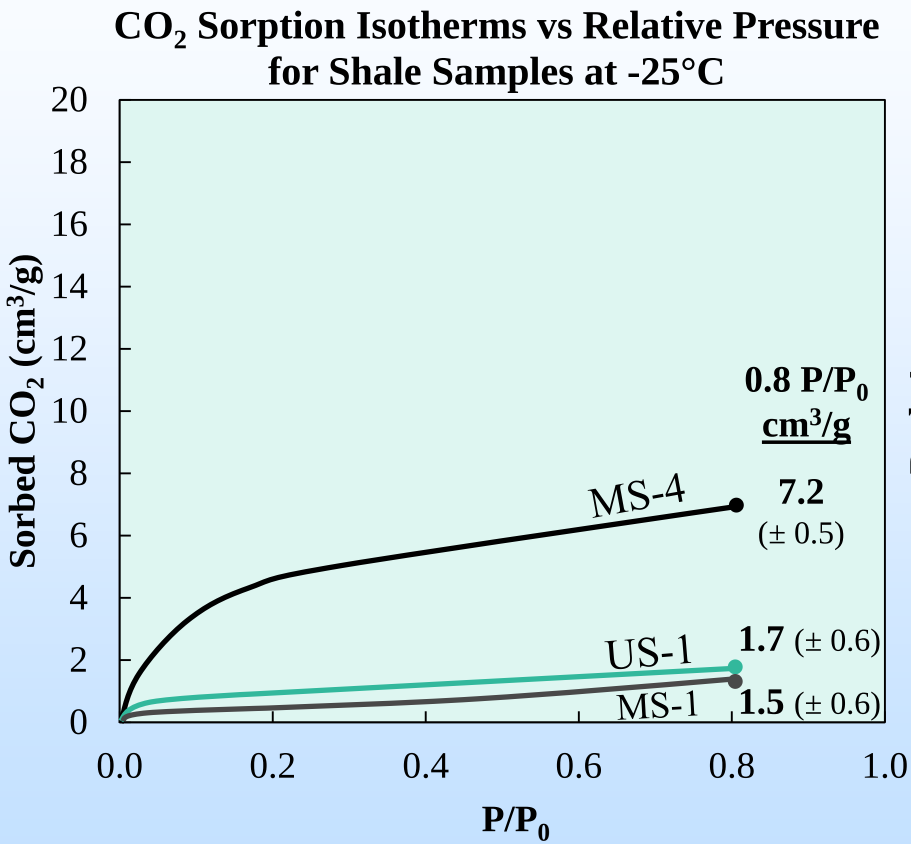
*measured at 40°C

Chemically Sorbed CO_2 IR Peaks: 1400, 830, 720 cm^{-1}

CO_2 Sorption on Shale Samples

CO_2 Sorption Isotherms:

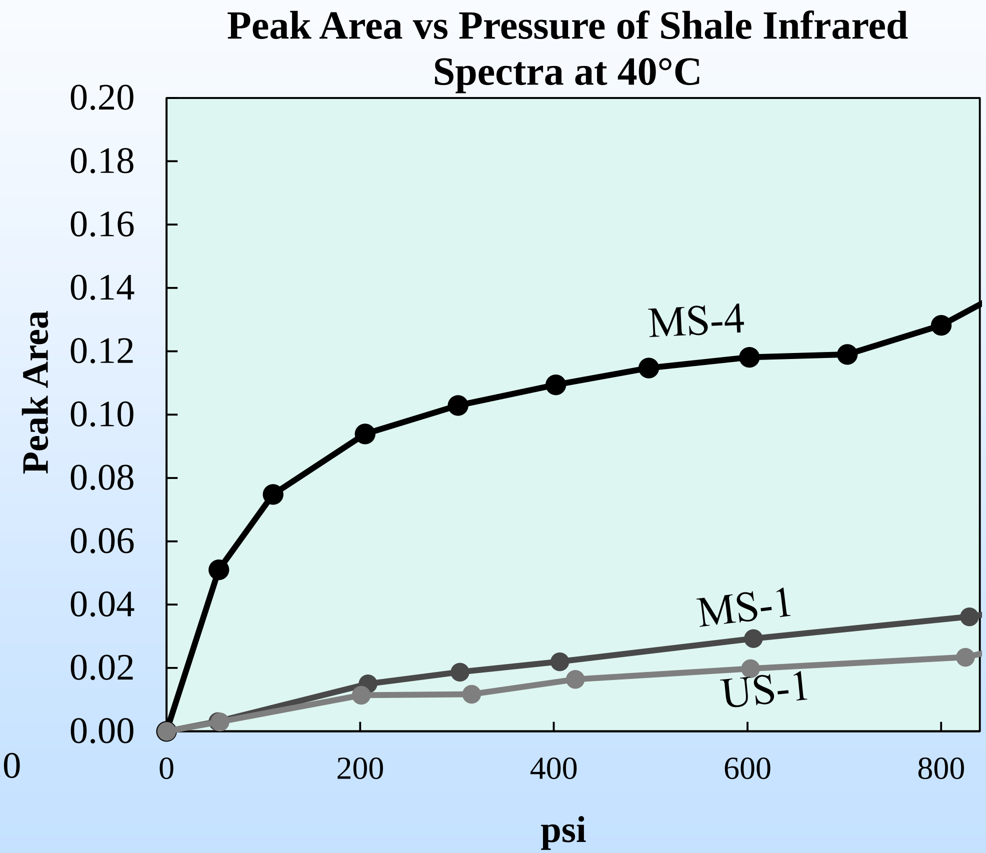
All Isotherm Data: 0-220 psi at -25, -15 & 0°C



MS-4 > US-1 ≥ MS-1

FT-IR Data:

Area of 2331 cm^{-1} CO_2 Sorption Peaks*



*2343 cm^{-1} peak not strong enough to obtain reliable area measurements

TOC-content (wt. %): MS-4 (9.2) > MS-1 (6.5) > US-1 (0.5)

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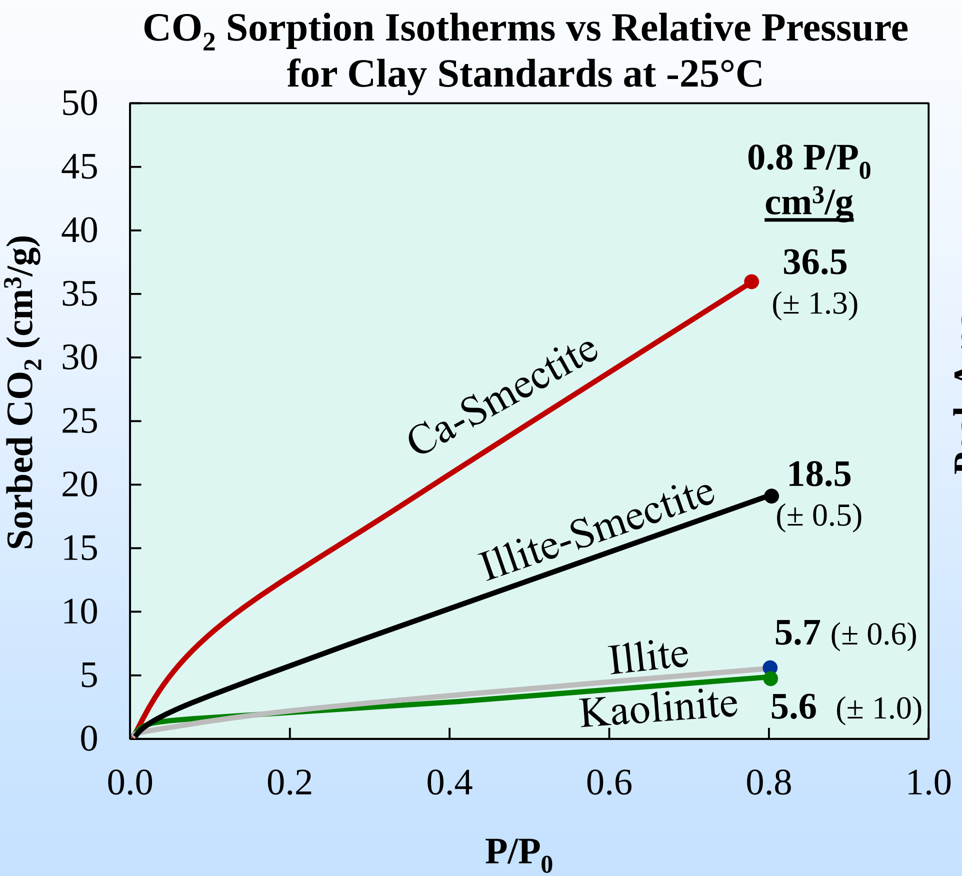
CO_2 Sorption on Clay Standards

CO_2 Sorption Isotherms:

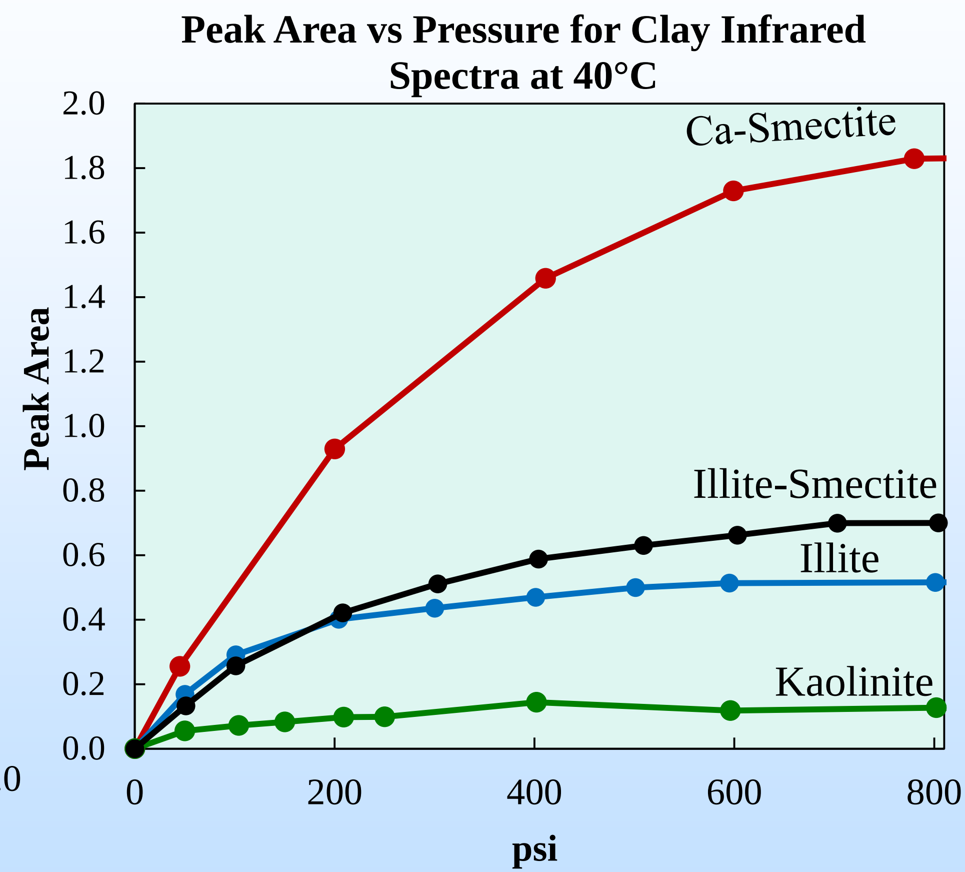
All Isotherm Data: 0-220 psi at -25, -15 & 0°C



Smectite > Illite-Smecite > Illite ≥ Kaolinite

FT-IR Data:

Area of 2343 cm^{-1} CO_2 Sorption Peaks



Integrated CO_2 peak area is not quantitative

FT-IR trends compliment results of CO_2 isotherm measurements

Experimental Analysis of CO_2 Storage in Organic-rich Shale

Results:

(1). Smectite > Illite-Smecite > MS-4 ≥ Illite ≥ Kaolinite > US-1 ≥ MS-1

Summary of CO_2 Sorption Isotherm Data at 0.8 P/P_0 & -25°C

Sample:	Smectite	Illite-Smectite	MS-4	Illite	Kaolinite	US-1	MS-1
cm^3/g	**36.5**	**18.5**	**7.2**	**5.7**	**5.6**	**1.7**	**1.5**
error +/-	1.3	0.5	0.5	0.6	1.0	0.6	0.6

(2). Two CO_2 sorption peaks observed at 2343 and 2331cm^{-1} on IR spectra of the shale samples (possibly also clays)

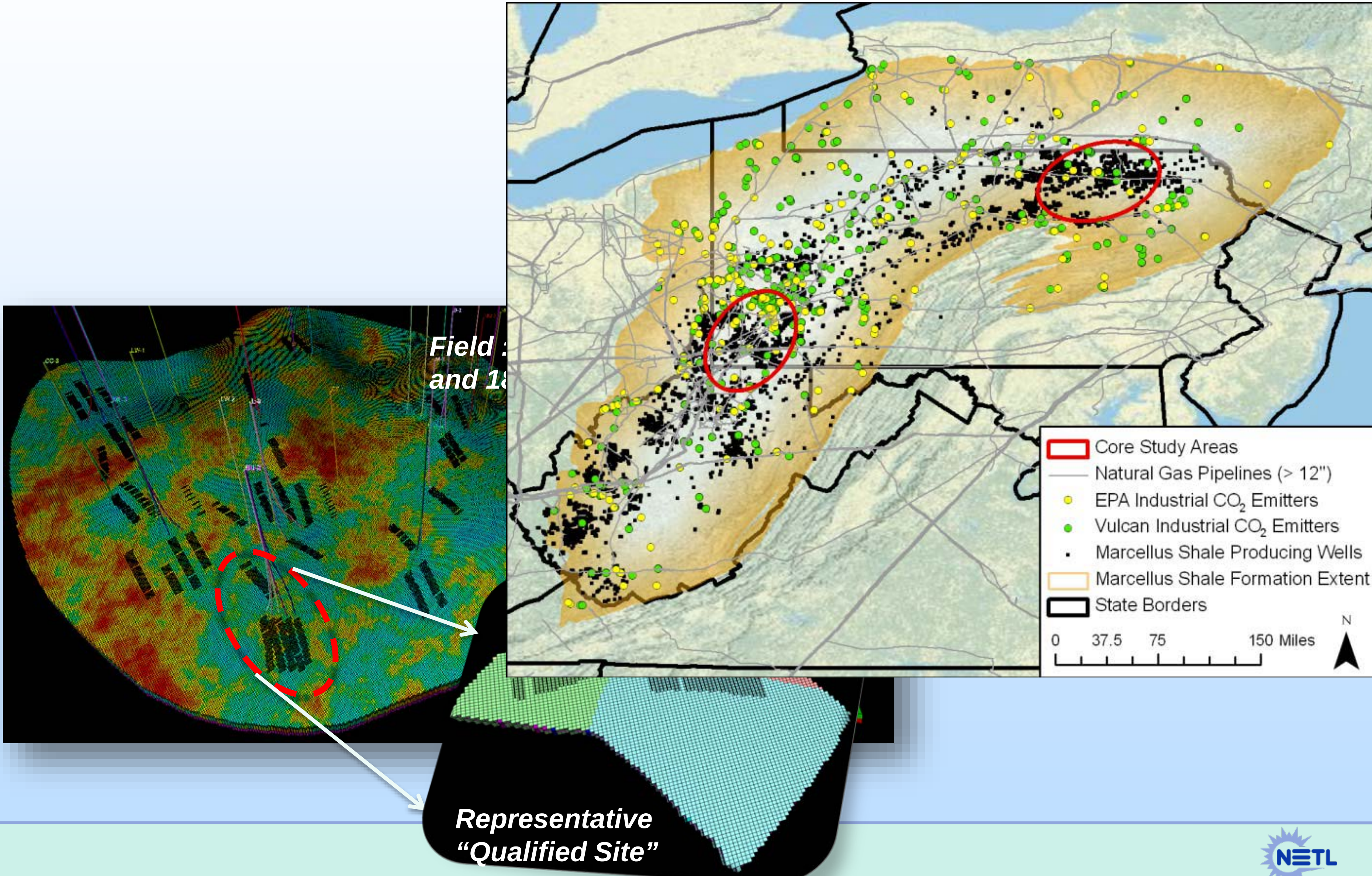
(3). No changes were observed in the IR spectra of clays or shales after 15 min of exposure to CO_2 at pressures between 0-800 psi and 40°C.

Interpretations:

(1). Shale formations with **high smectite, illite-smectite, and/or high TOC-content** may have high CO_2 storage potential (*e.g. Busch et al., 2008; Busch et al., 2009; Ross and Bustin, 2009*)

(2). There may be two CO_2 sorption sites in shales & clays: in the interlayer* of clay structures & in the interpore space of minerals & kerogen. (**e.g. Rother et al., 2012; Geisting et al., 2012; Loring et al., 2012*)

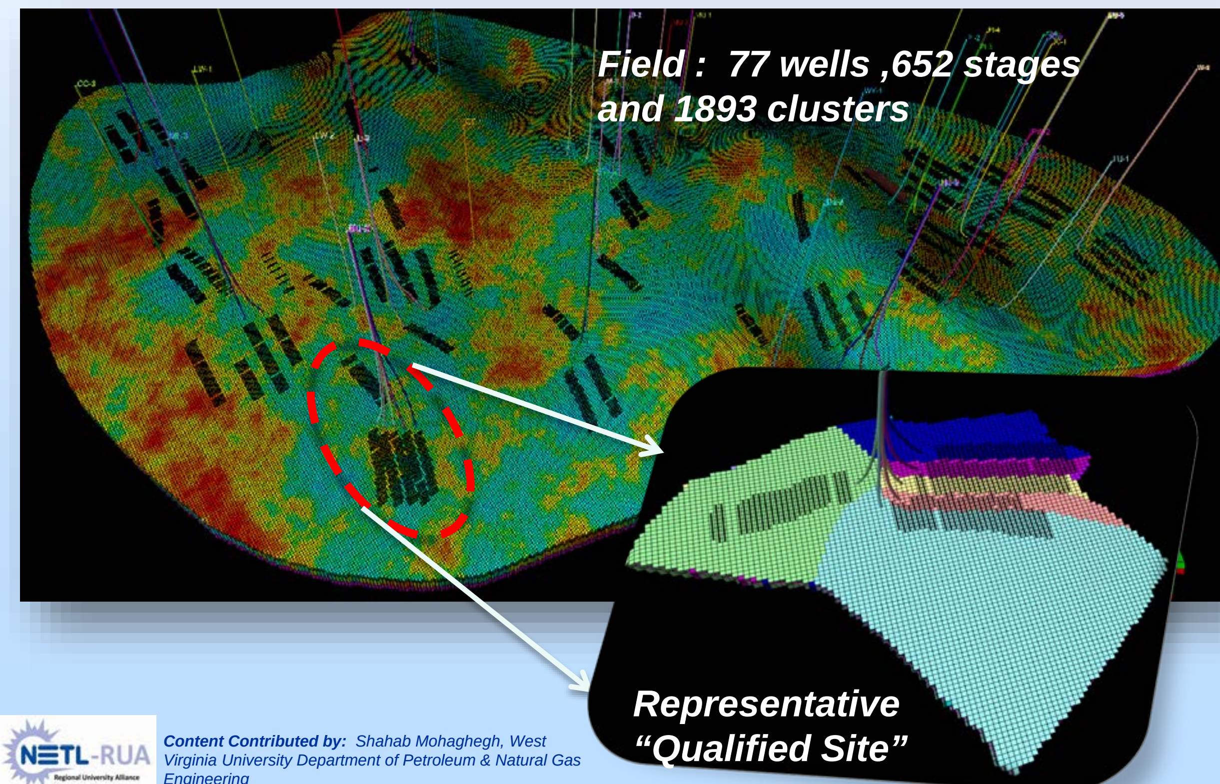
(3). At experimental conditions, **exposure to CO_2 does not induce chemical changes** in clays & shales of these compositions

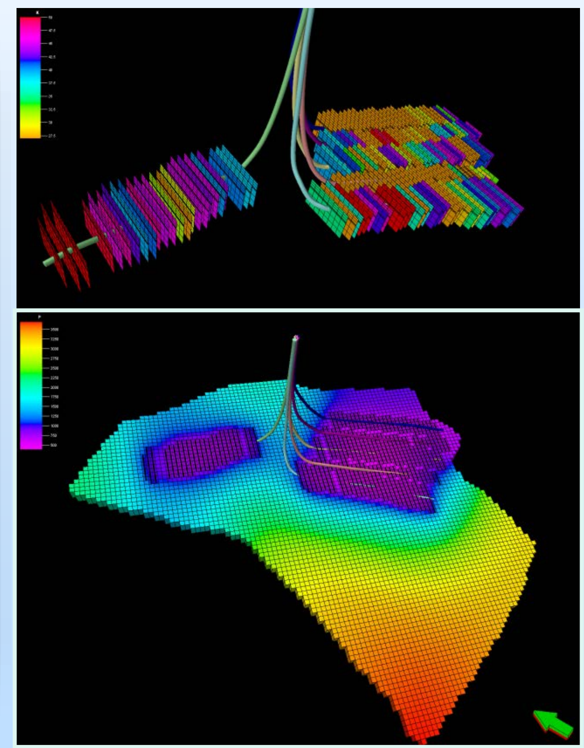

Field
and
Core Study Areas
Natural Gas Pipelines (> 12")
EPA Industrial CO_2 Emitters
Vulcan Industrial CO_2 Emitters
Marcellus Shale Producing Wells
Marcellus Shale Formation Extent
State Borders
0 37.5 75 150 Miles
N
Representative
"Qualified Site"

CO_2 Storage in Depleted Shale

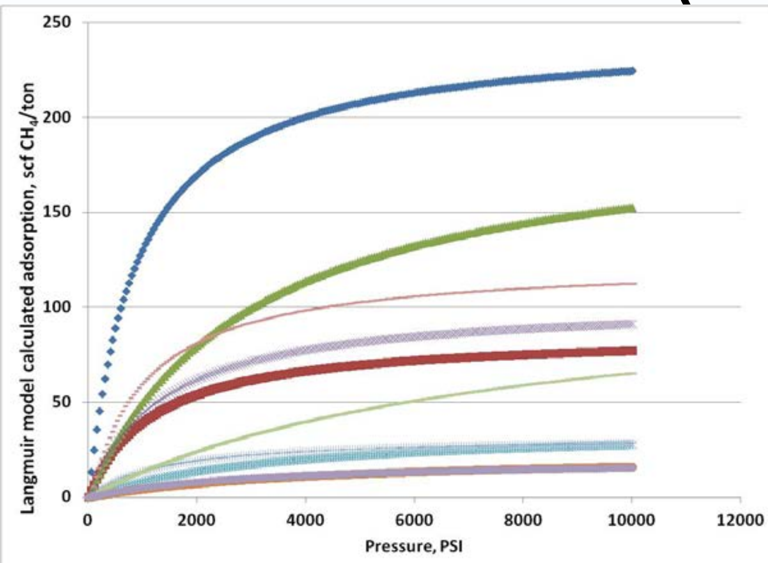
combining conventional/AI-based reservoir modeling

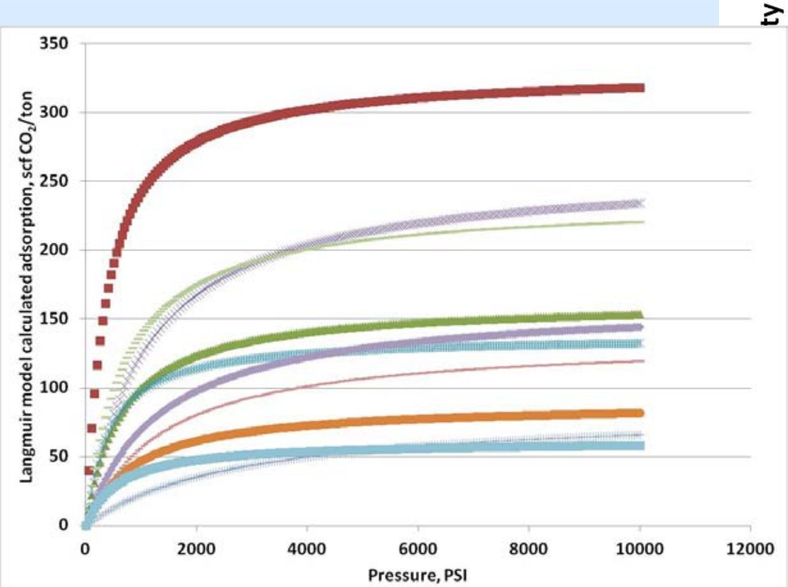
- Acquire real data on gas production from a set of shale gas wells
- Use that set of data to develop population statistics
- Develop a history-matched model of shale gas production (29 month production history) using a conventional reservoir model
- Project forward to economic limit before initiating CO_2 injection
- Develop a surrogate reservoir model based on the history matched model to predict wellpad performance under CO_2 loading



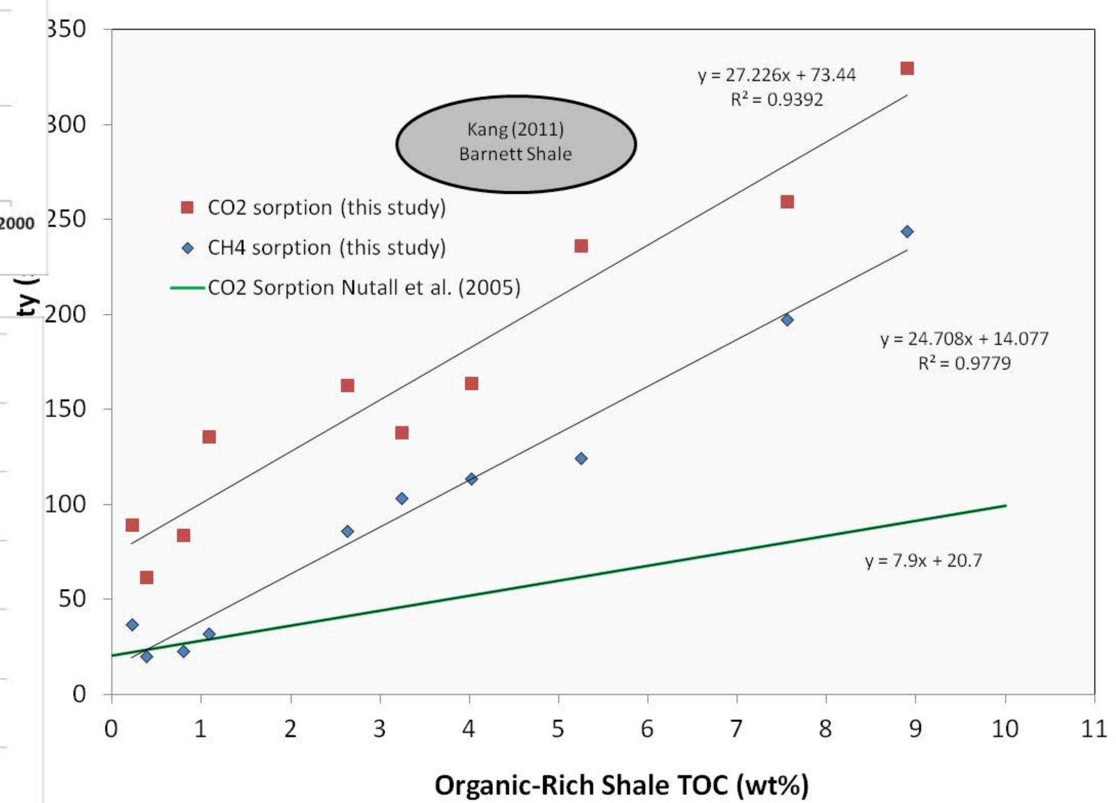


CO_2 and CH_4 Sorption capacity as function of %TOC (single-fluid isotherms)





- Sorption capacity of CO_2 and CH_4 exhibit linear relationship withTOC



N… *f Devonian Black Shales for Potential Carbon Dioxide Sequestration and Enhanced Natural Gas* P… ey, University of Kentucky, for the U.S. Department of Energy, National Energy Technology Laboratory, December 30, 2005