A Coupled Geomechanical, Acoustic, Transport and Sorption Study of Caprock Integrity in CO_2 Sequestration

DE-FE-23223

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U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Transforming Technology through Integration and Collaboration

August 18-20, 2015

Agenda

- Objectives and motivation
- Initial work and error analysis
- Adsorption setup and measurement protocol
- Accomplishments to date
- Permeability and acoustics measurements; simulations
- Future work

Background

- Carbon capture and storage in deep geological settings
- Caprock seals and prevents buoyant migration of CO_2
  - Permeability of caprock ~ Nanodarcy
  - Permeability of tight-gas shales ~ Nano to Microdarcy
- CO_2 injection changes the state of stress in reservoir rocks and in caprocks
- **Could faults or fractures develop in caprocks that allow CO_2 transport and escape?**

Hypothesis and Objectives

Hypothesis:

- Mechanical damage to shales does not necessarily lead to high permeability and substantial leak rates

Objectives:

- Determine the behavior of intact and fractured caprocks when exposed to supercritical CO_2 at elevated pressures
- Quantify adsorption, strain and acoustic properties of shales with sorbed CO_2
- Provide framework for monitoring, verification and accounting (MVA) efforts of CO_2 sequestration and its effect on caprock

Accomplished to Date

Completed:

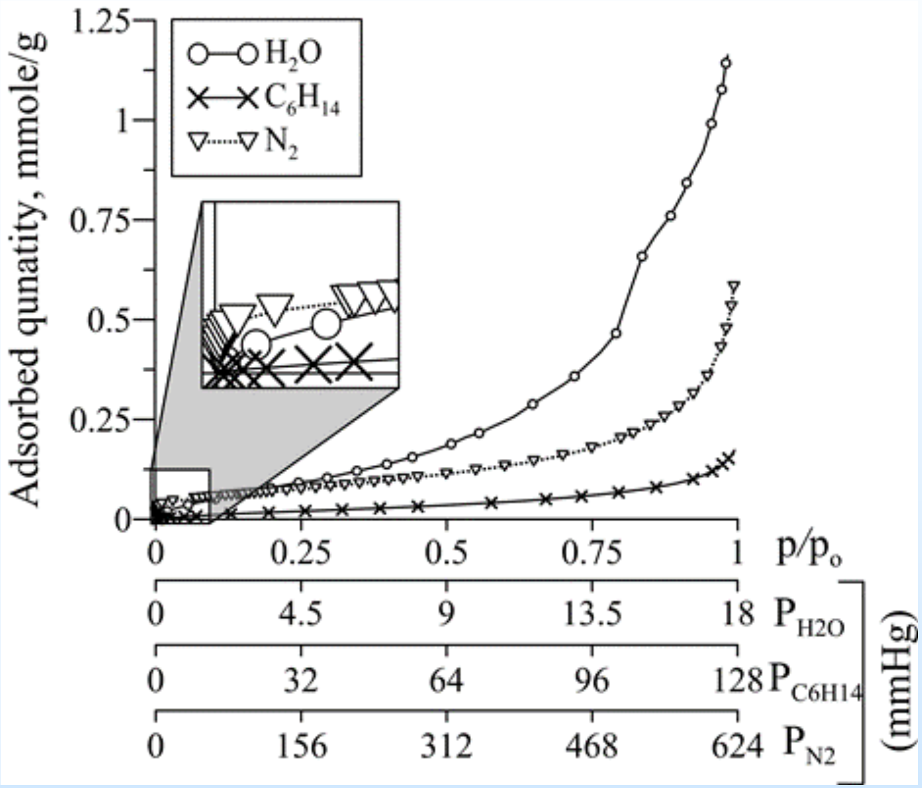
- Experimental Design Protocol
- Subcritical Adsorption on various fluids
- Sample Selection and Acquisition
    - Organic-Rich Shales:
        - ***Eagleford***
        - ***Bakken***
        - ***Utica***
    - Non-Organic-Rich Shales:
        - ***Mancos***

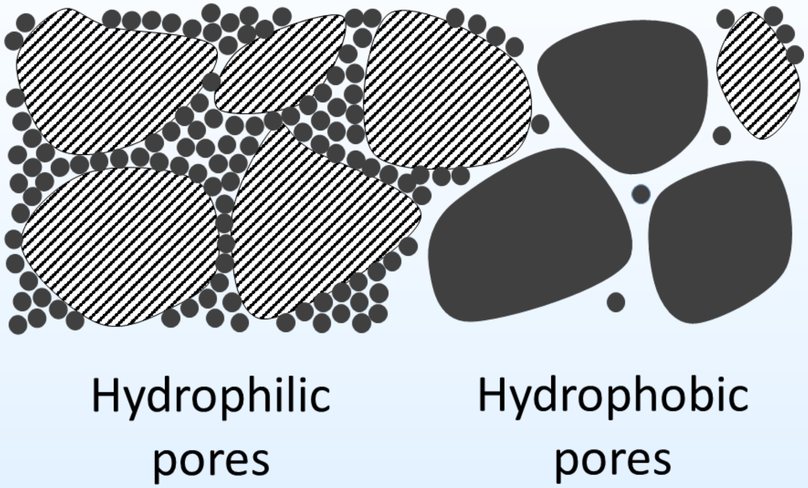
Ongoing:

- Acoustic Tests
- Equation of state calculations
- High pressure and temperature tests
- Triaxial tests for strength and fracture permeability

Motivation

Preferential sorption of fluids depends on polarity of surfaces

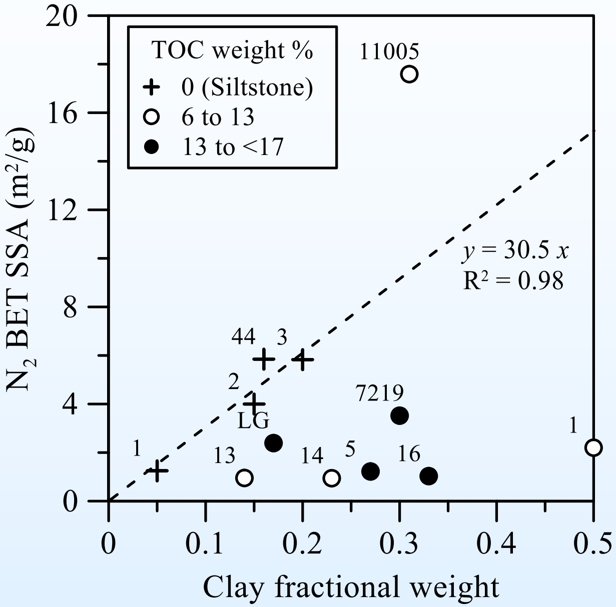




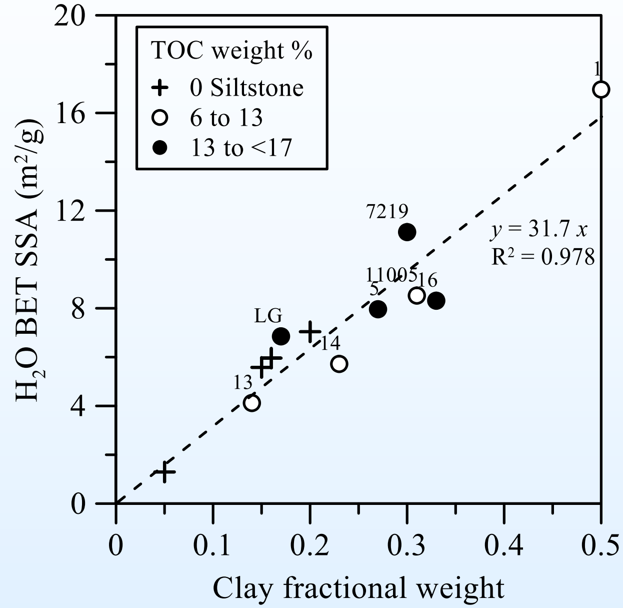
- Quantification of hydrophilic and hydrophobic pores of shales

Surface Area and Clay Content

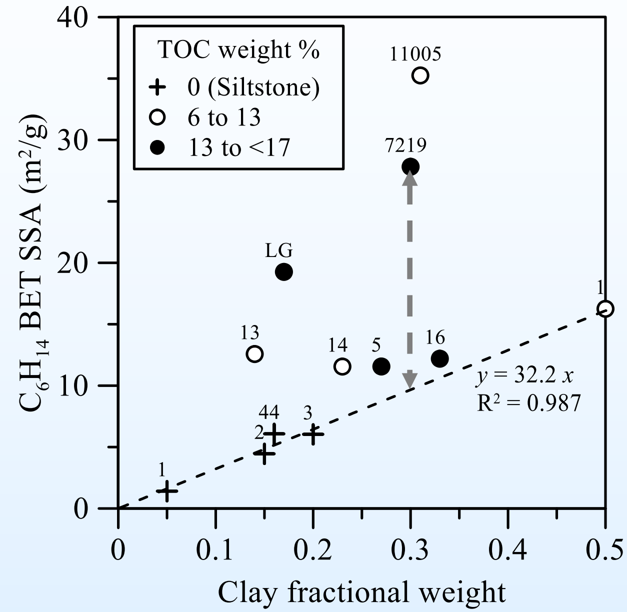
Nitrogen



Water



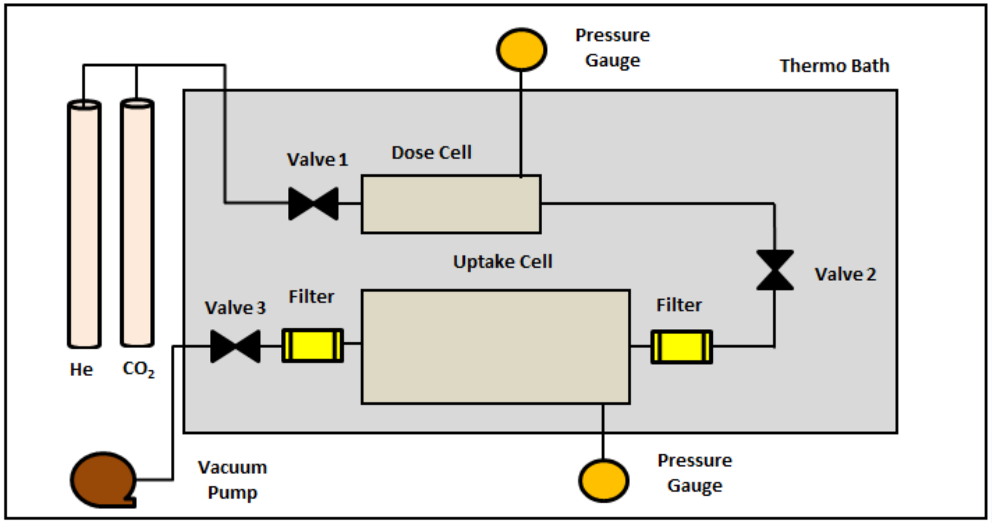
Hexane

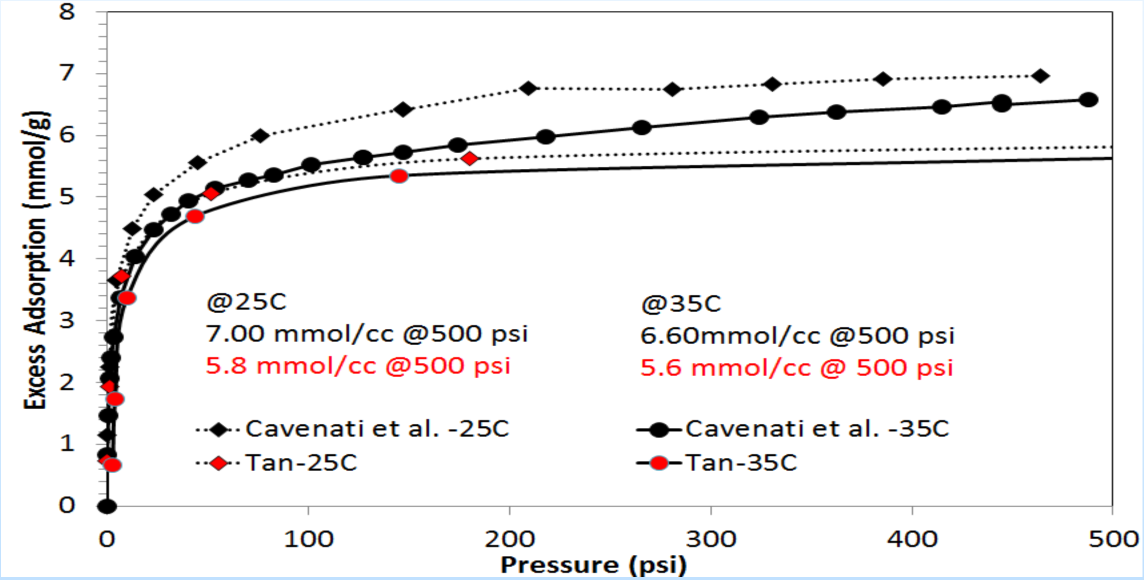


- Cryogenic N_2 is selectively blocked by nano-sized pores in the organic matter
- OM pores are hydrophobic
- OM pore development starts at the onset of oil window
- Presence of **bitumen free OM pores**

Prototype and Initial Measurements

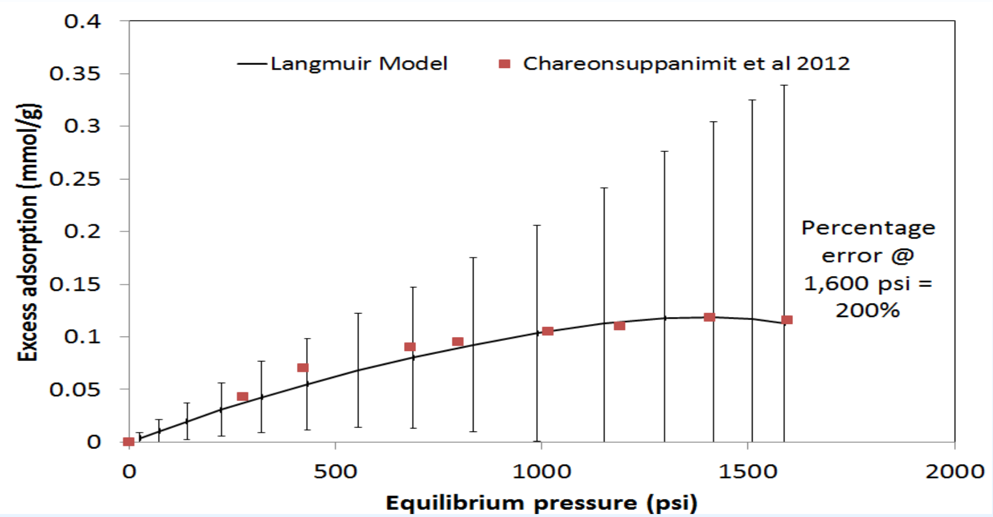
Manometric system designed to test CO_2 adsorption on synthetic 13X zeolites





CO_2 adsorption at 25-35 °C up to 500 psi was measured and compared to literature

Error Analysis



System Properties

Isotherm temperature: 140 °C

Volume of RV=65ml

Volume of SV=65ml

Sample Properties

Porosity: 10%

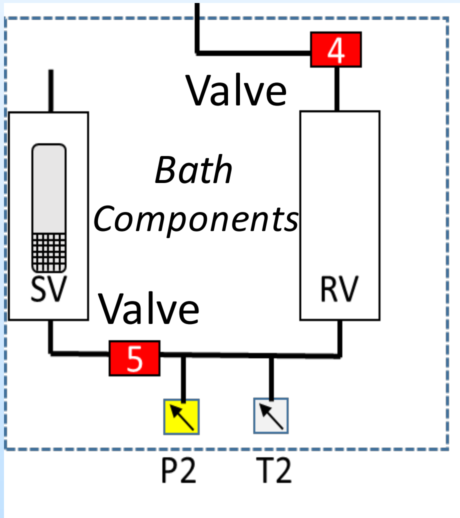
Grain density: 2.7 g/cc

Langmuir Parameters:

b: 0.01

V_{max}: 40 SCF/ton

Assuming connection volume to be zero

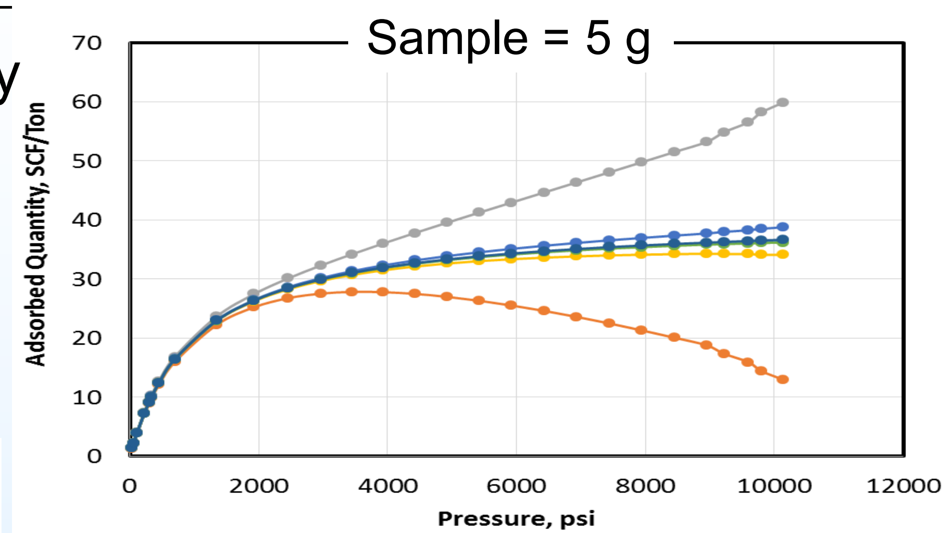


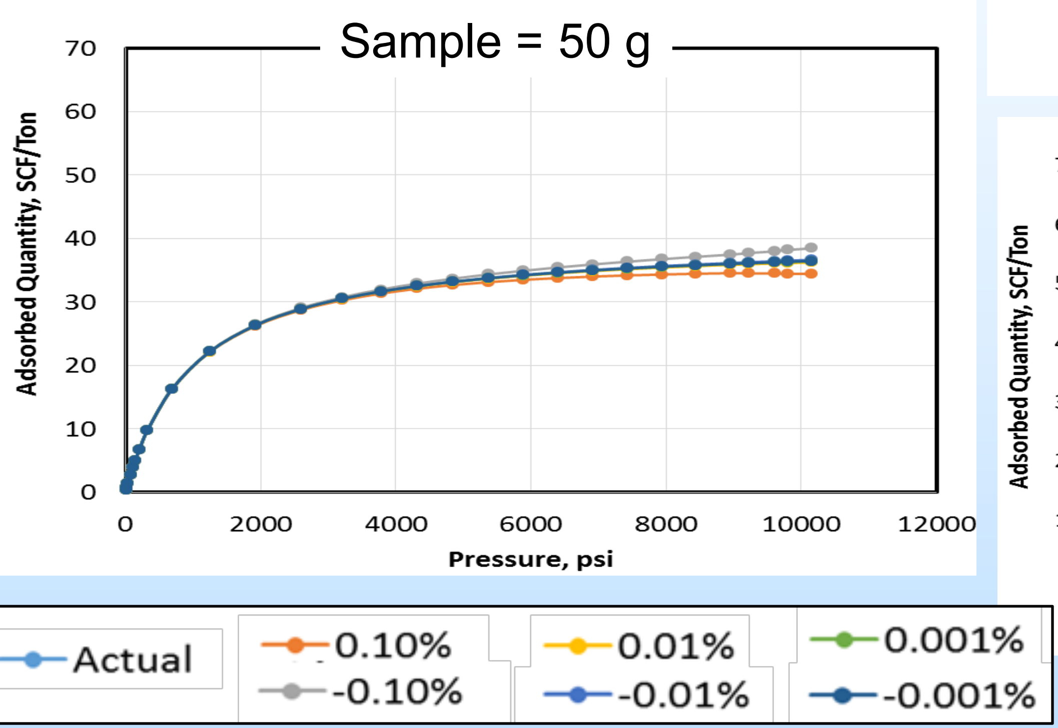
Sample Mass (g)	V_{SV}
1	64.6
5	63.1
20	57.6
50	46.5
100	28.0

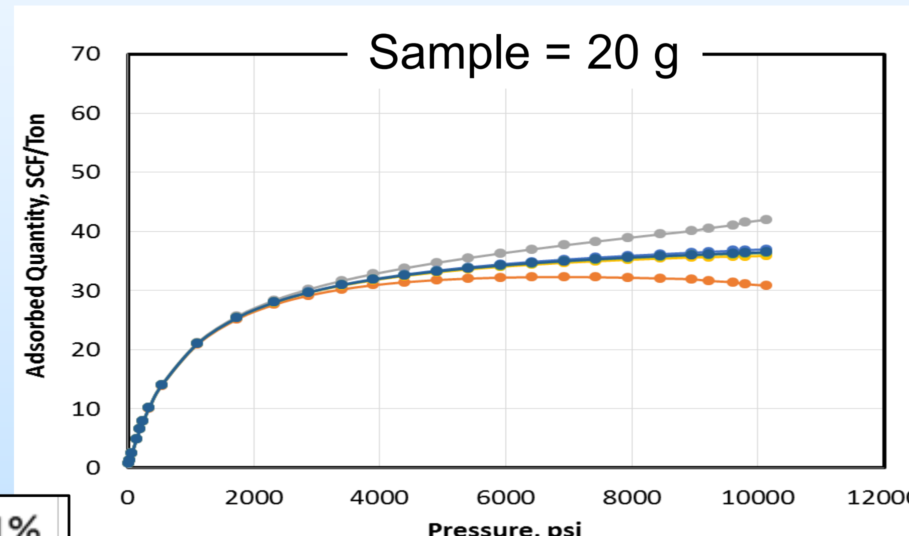
Error Analysis for Transducer Selection

Earlier prototype: 0.25% Tx accuracy

Error analysis: need Tx accuracy= ***0.01%*** for reliable high pressure isotherm results



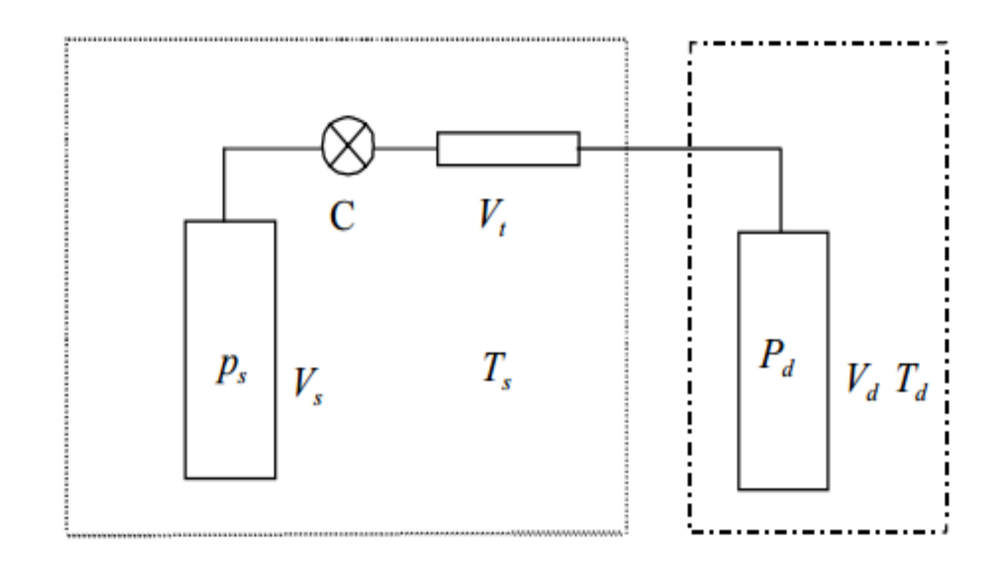




Adsorption Experiment Setup

Working Principle:

- Volumetric type apparatus
- Performs adsorption and desorption measurements by precisely recording pressure



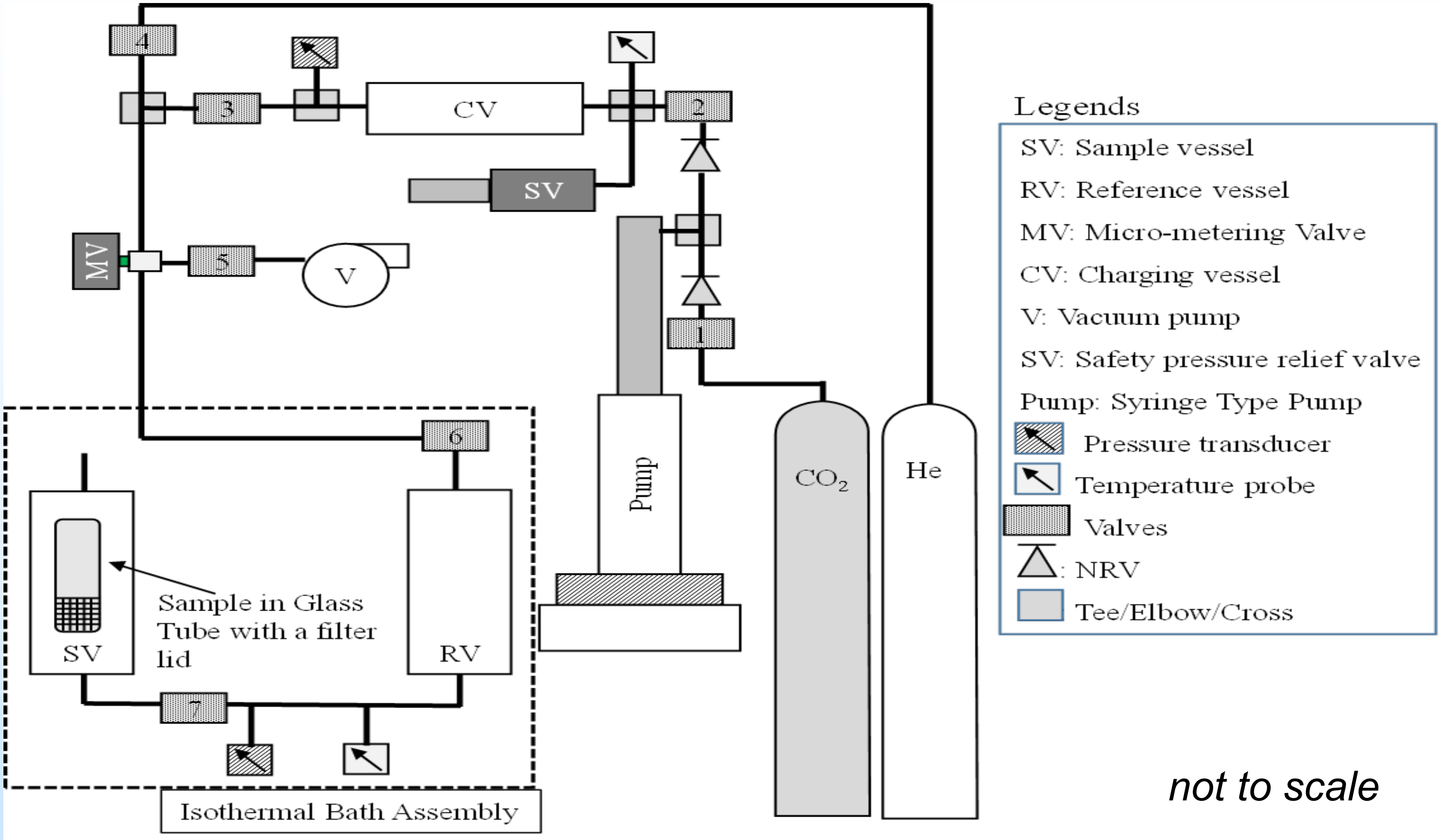
Material Balance:

$$n_1 = \frac{p_s V_s}{z_{(p_s,T_s)} R T_s} + n' + n''$$

$$n_2 = p_A \left[\frac{V_s}{z_{(p_s,T_s)} R T_s} + \frac{V_c}{z_{(p_s,T_c)} R T_c} + \frac{V_A}{z_{(p_s,T_A)} R T_A} \right]$$

$$n_e = n_1 - n_2$$

Experimental Design

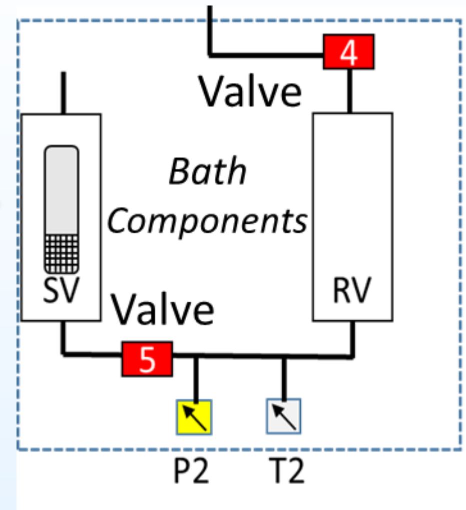


Schematic illustration of the supercritical adsorption apparatus

Measurement Protocol

Determine SV and RV volumes by free space procedure

Components at vacuum → Valve 4 opens → Valve 4 closed when P2 reads around a predetermined value → When equilibrate, read $P_{RV,1}$ → Valve 5 opens → When equilibrate, reads $P_{SV,1}$



Initial number of free molecules (Valve 5 closed): $$n_1 = \frac{P_{RV,1} V_{RV}}{Z_{(P_{RV,1},T_{Iso})} R T_{Iso}}$$

Final number of free molecules (Valve 5 open): $$n_1' = \frac{P_{SV,1}\{V_{SV} + V_{RV}\}}{Z_{(P_{SV,1},T_{Iso})} R T_{Iso}}$$

Number of adsorbed molecules in the system: $n_1^{ads} = n_1 - n_1'$

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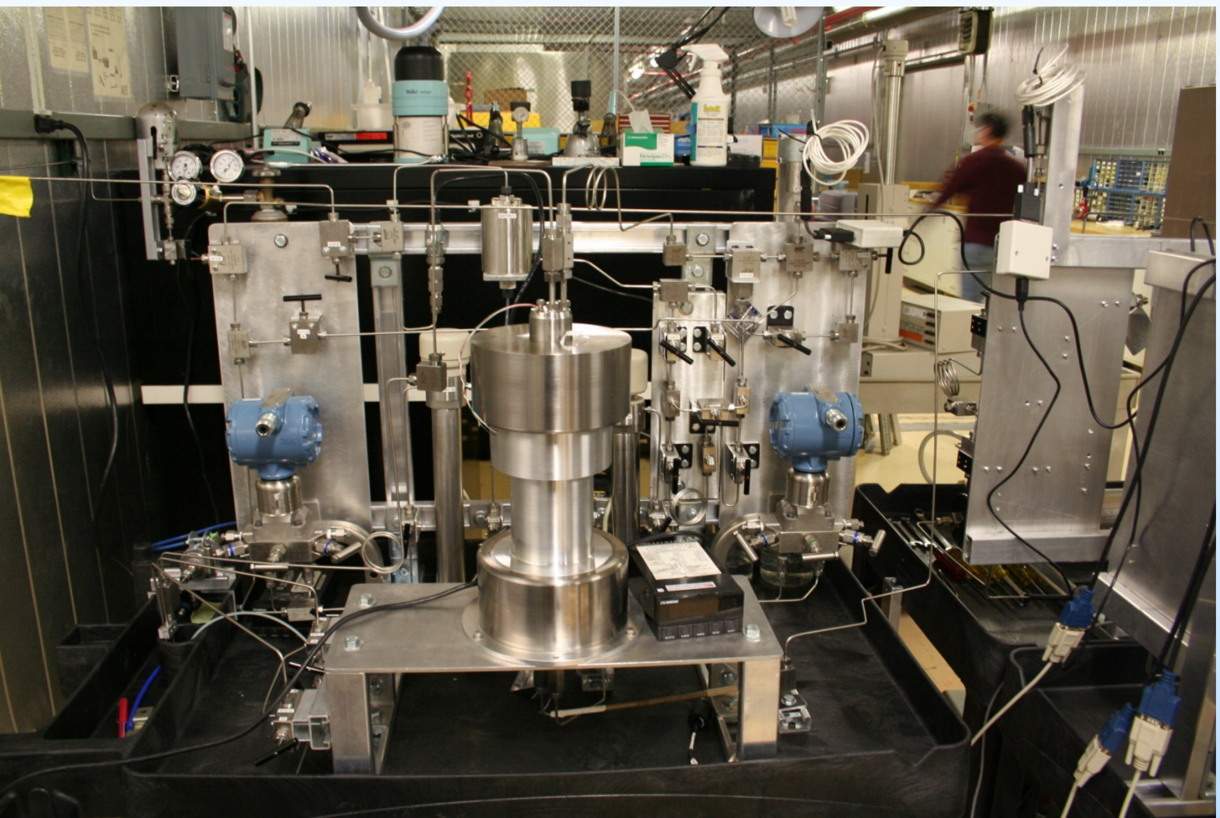
In Situ Permeability Measurements

- Triaxial coreflood studies coupled with x-ray tomography
  - New and unique LANL capability
  - Deformation modes: Compression, direct shear, and tensile fractures



- Experimental Limits

  Max Pressure: 5000 psi
  34.5 MPa

  Max Temperature: 212 °F
  100 °C

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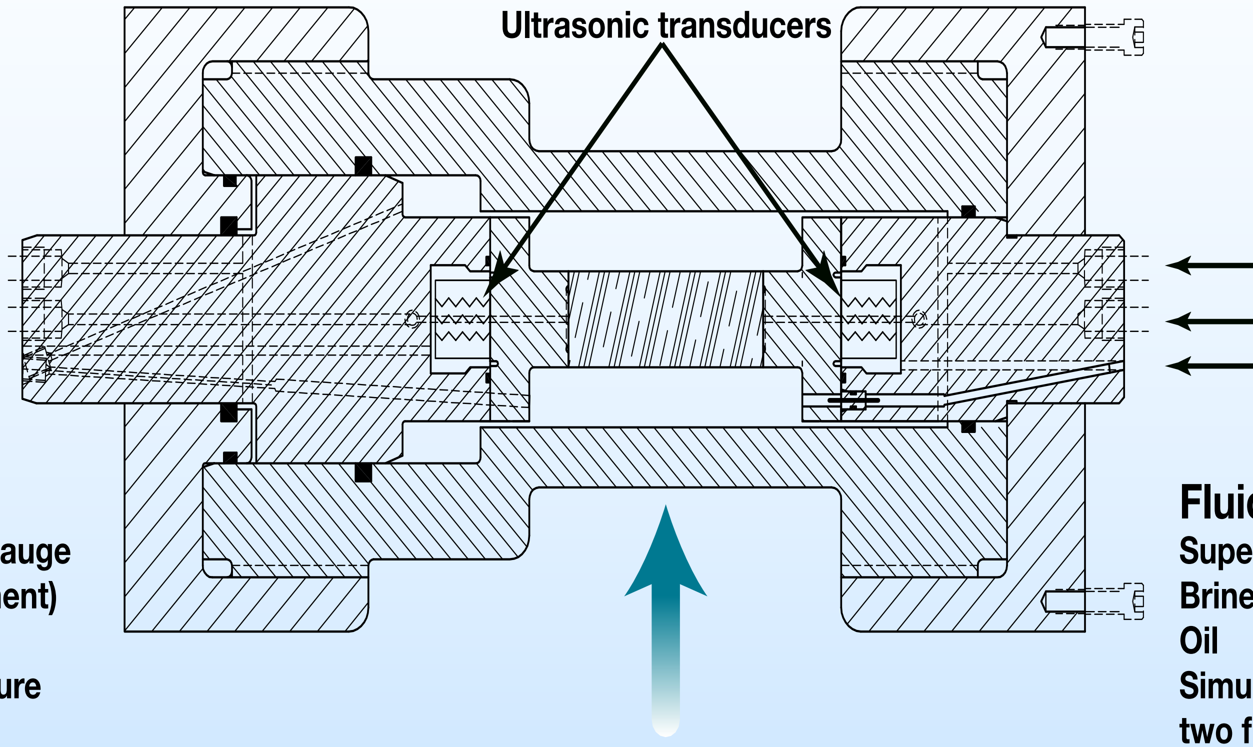
Triaxial Experimental System

Triaxial System: Independent Pore, Confining and Axial Pressure



Neutron or X-ray Tomography

Measurements:

Deformation (strain gauge and piston displacement)
Permeability
Pressure & Temperature
Acoustic velocity
Acoustic emission
Fluid samples

Fluids:

Supercritical CO_2
Brine
Oil
Simultaneous injection of two fluids

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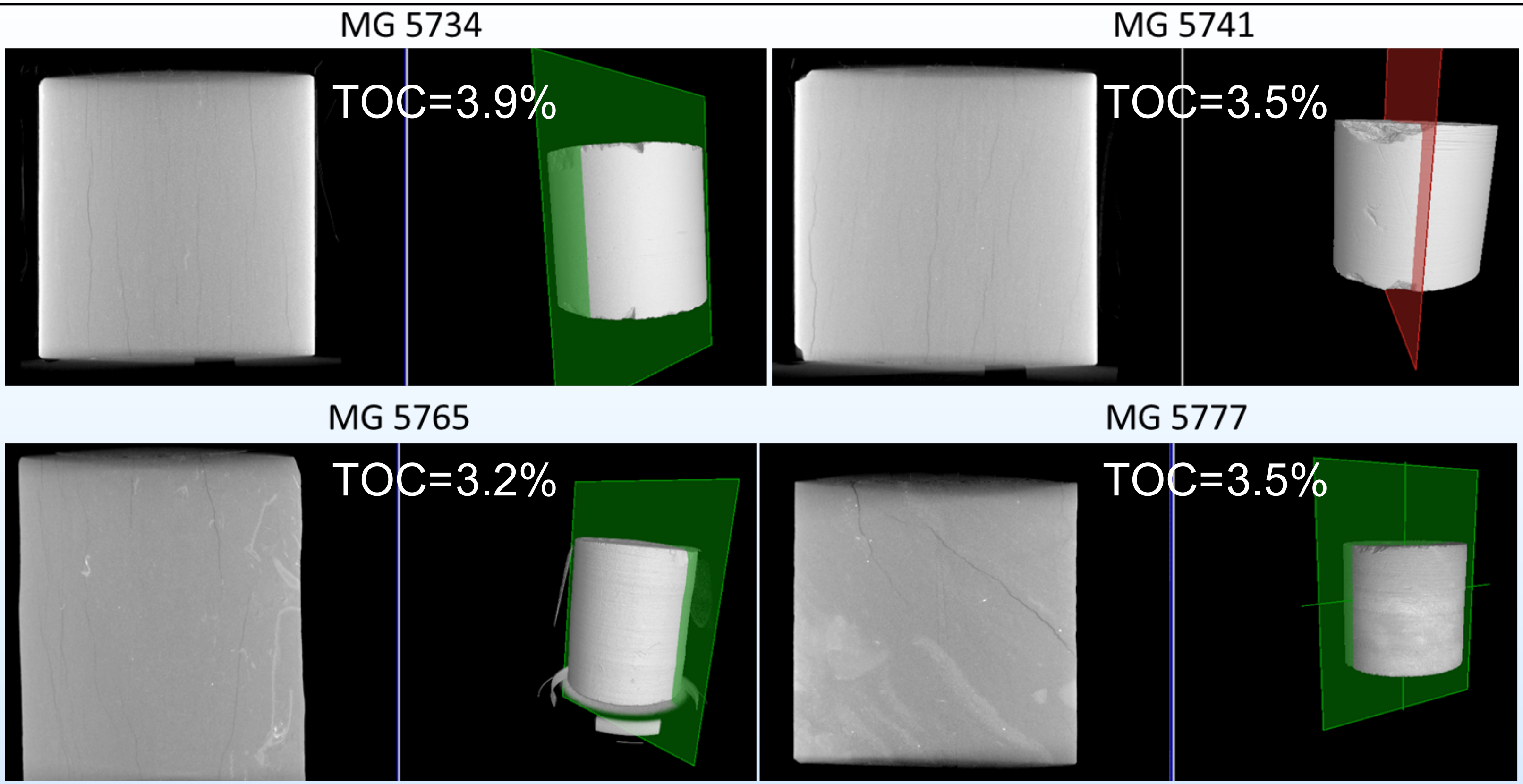
Pre-Experimental Tomography



- Utica Shale provided by industrial partner Chesapeake Energy
- Mudstones (contain both clay and carbonates)
- Core were oriented both vertically and horizontally

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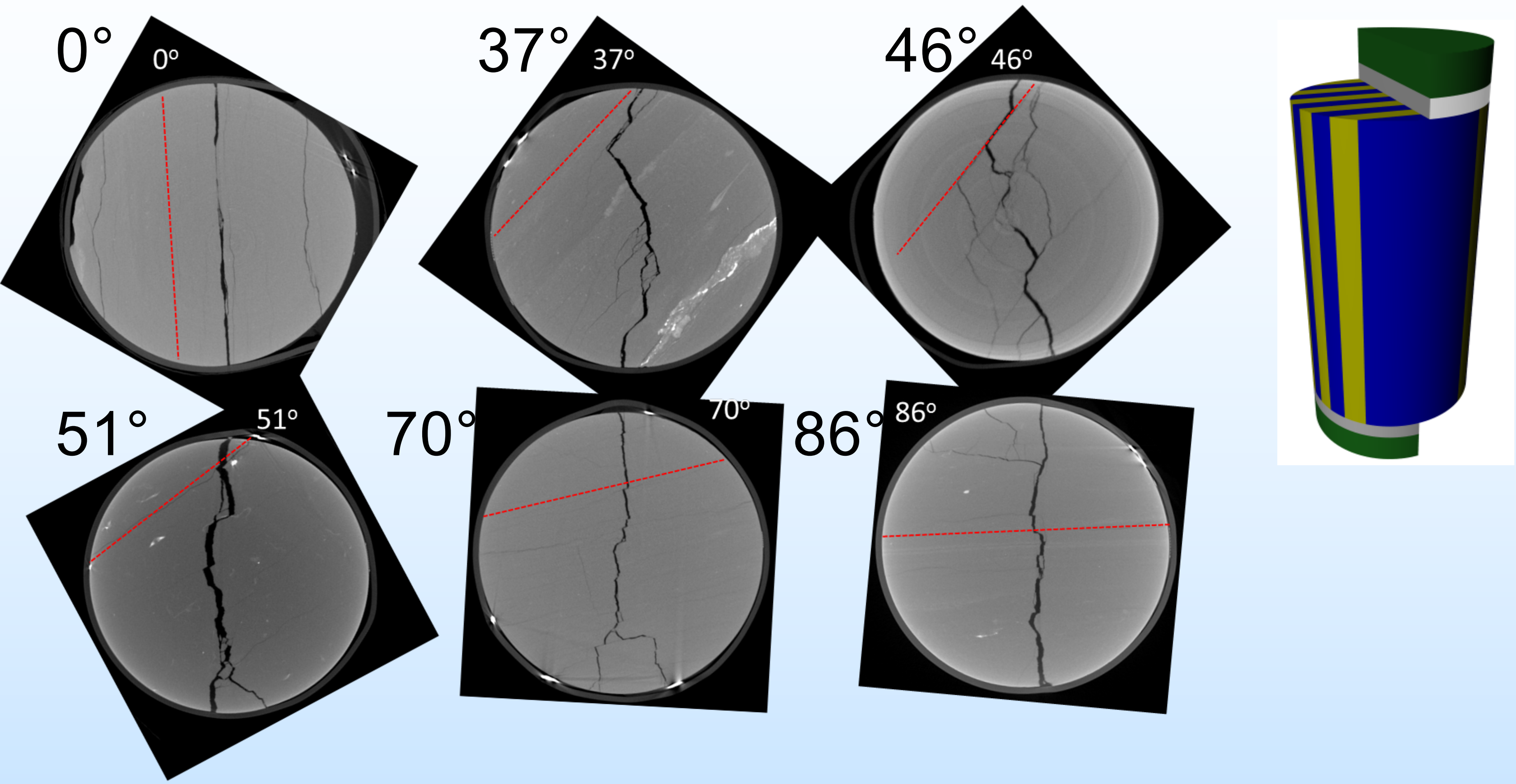
Fracture Permeability Studies



As a function of shear-plane to bedding-plane angle

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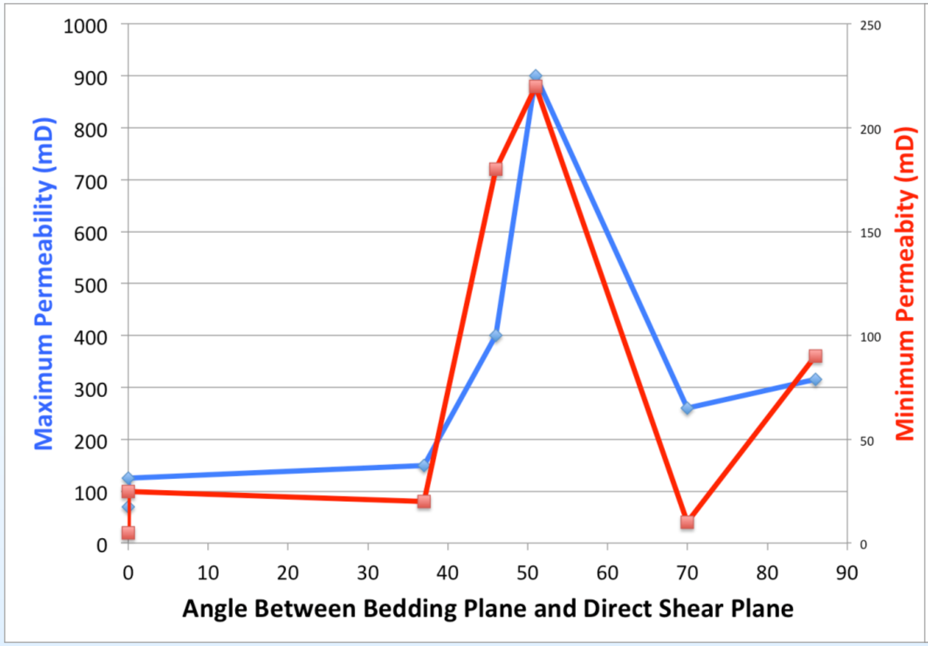
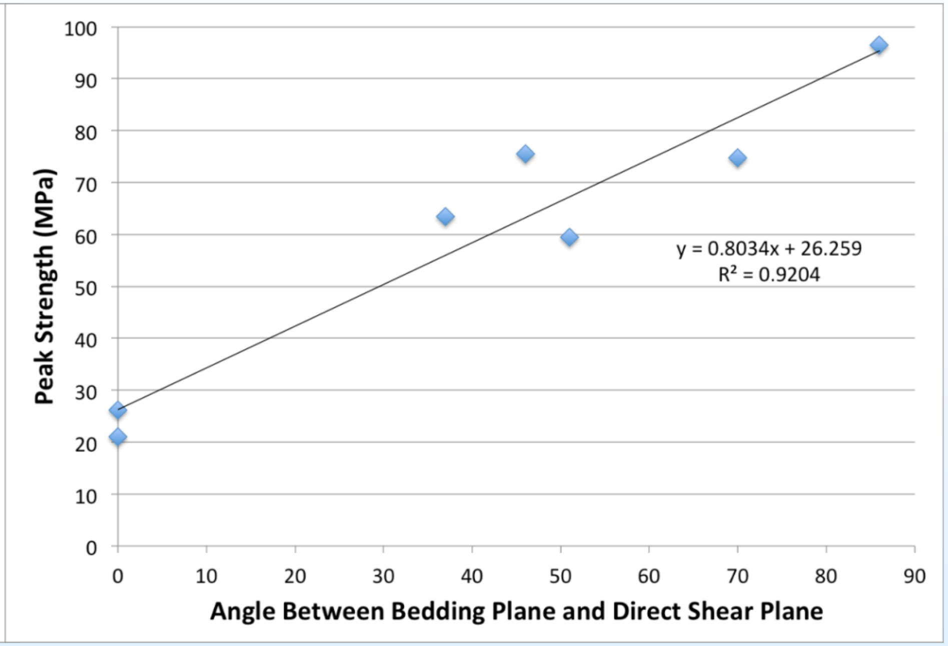
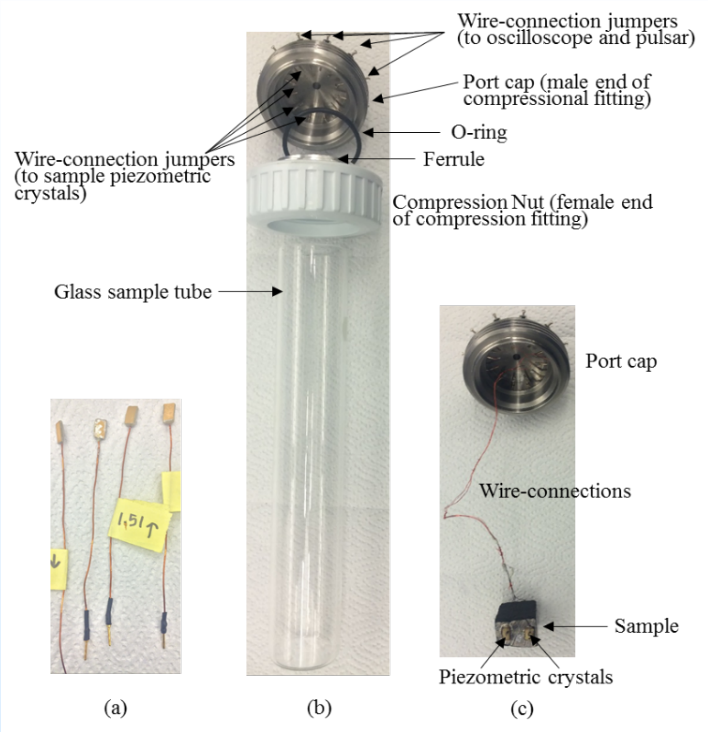
Fracture Permeability Studies

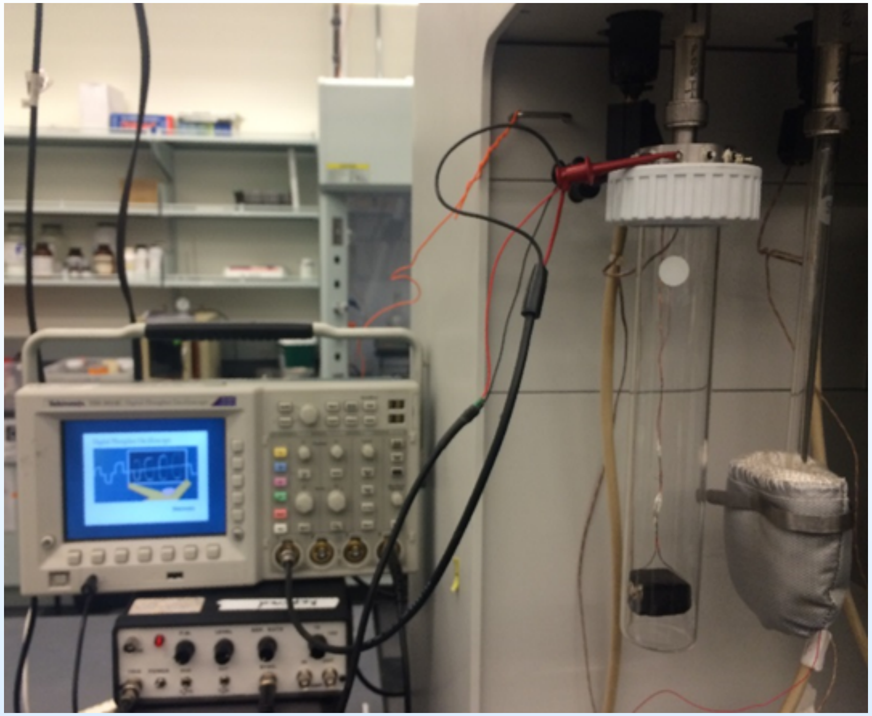




- Permeability peaks as fractures cross bedding at 45°
- Strength is a linear function of bedding plane angle

Acoustic Measurements



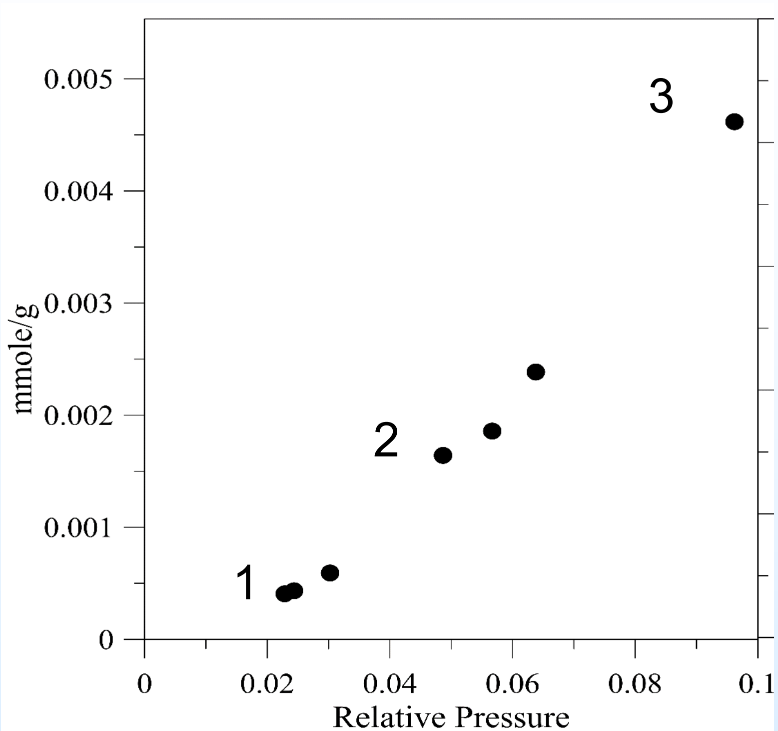


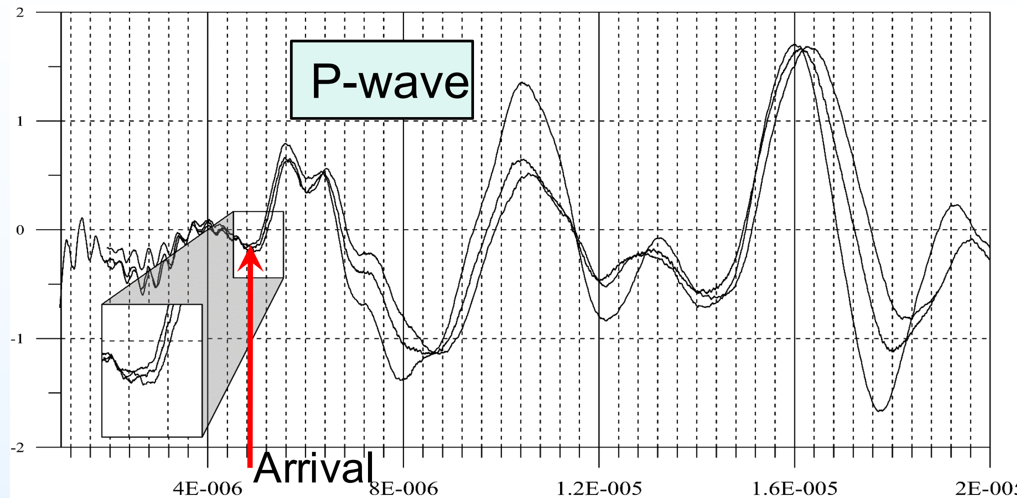
Simultaneous acoustic and resistivity measurements during CO_2 sorption

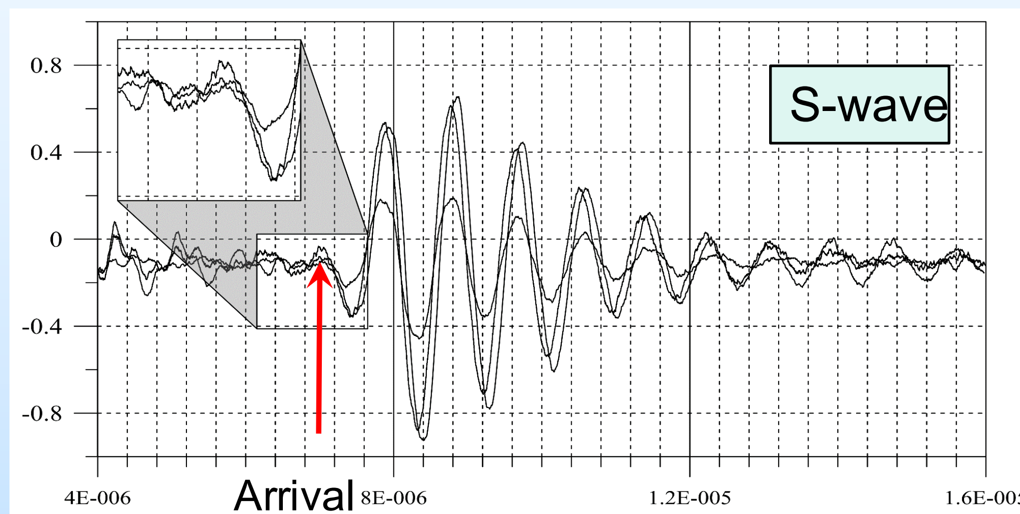
Plan also for simultaneous acoustic and resistivity measurements with NMR relaxation times

S. Kumar

First Subcritical Measurements







- 1, 2 and 3 indicate isotherm points at which acoustic measurements were taken

Theoretical Models

Experimental setup	Finite volume	Modified finite volume
Diffusion model	Micro-pore controlled	Macro-pore controlled
Sorption isotherm	Langmuir isotherm for Zeolites	

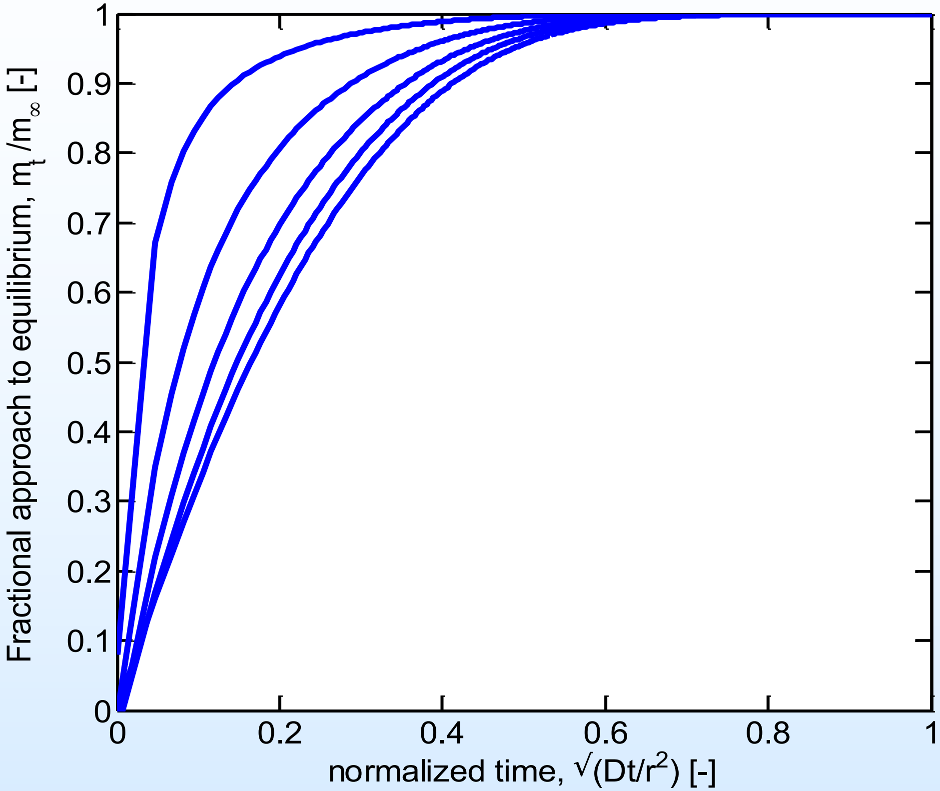
Analytical Model

SOL Model

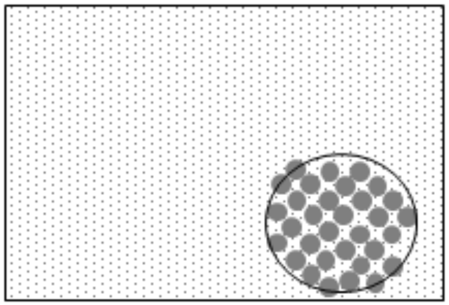
POR Model

(SOL Model and POR Model:) Derived from material balance

Theoretical Models

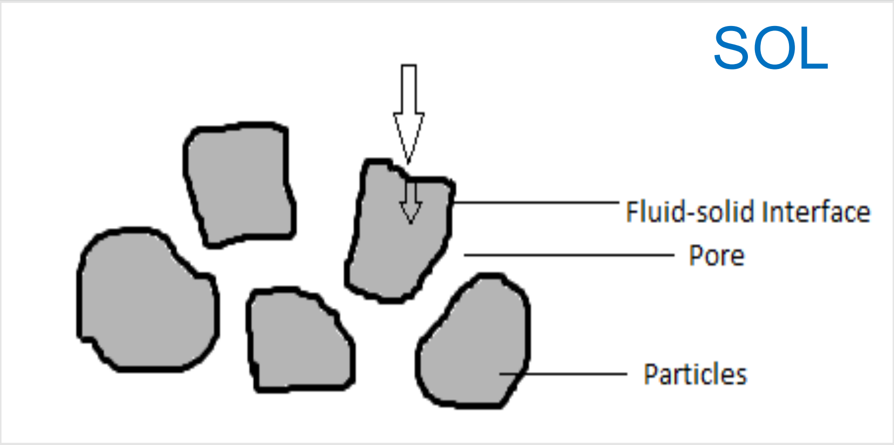


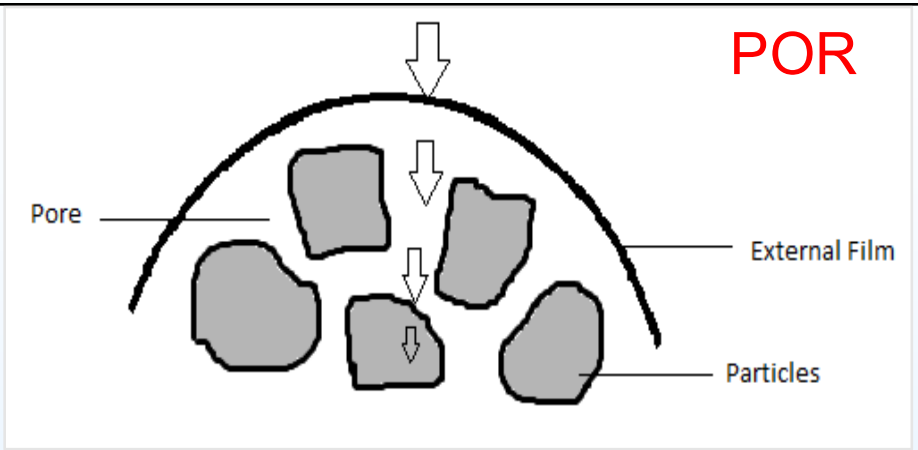
Finite volume diffusion model fractional uptake curve as increases, reproduced from Crank 1987



- Simple analytical model for **micropore** controlled diffusion
- Applied to manometric apparatus (neglect valve influence)
- Dosing reservoir and uptake reservoir at equilibrium
- Ideal gas assumed

Diffusion Models





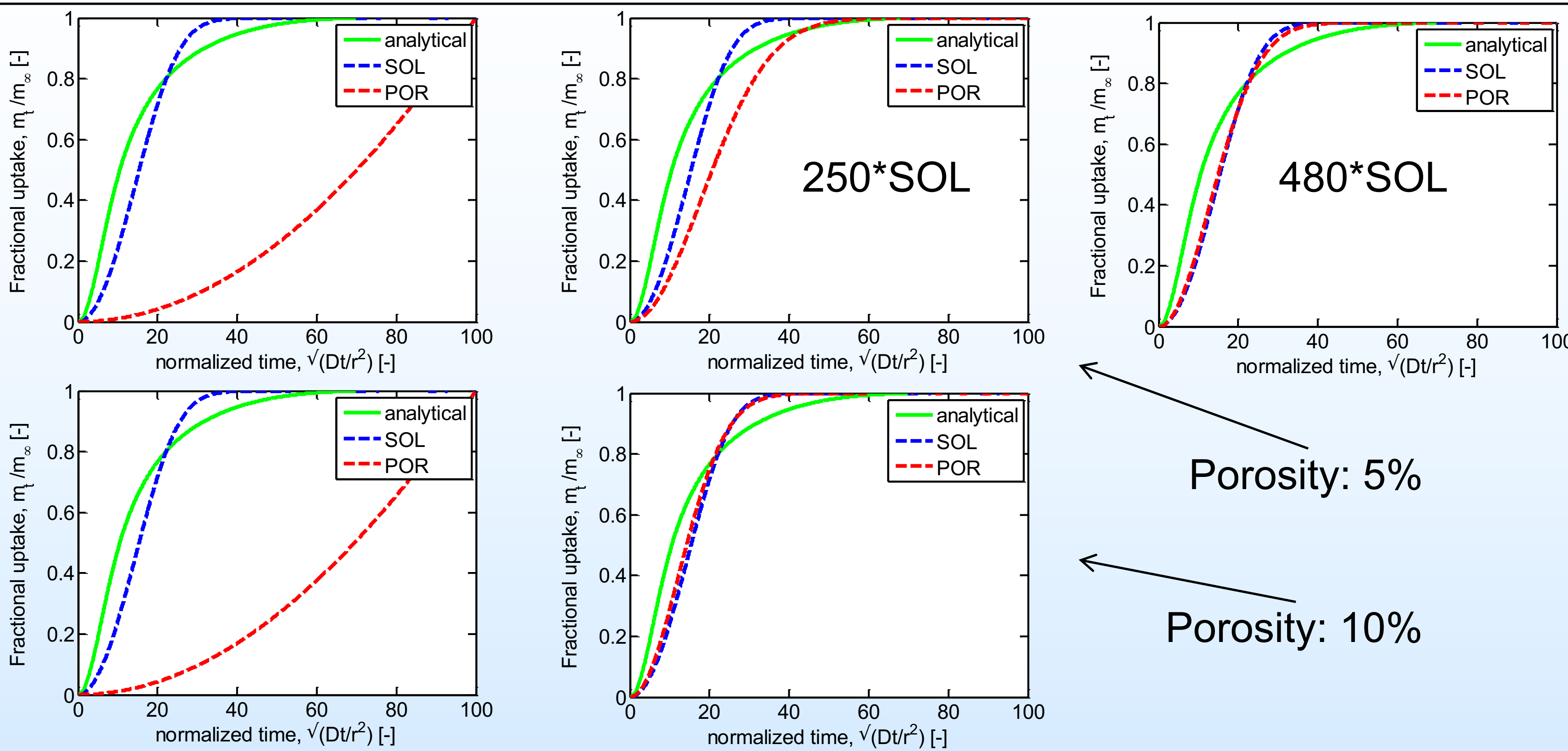
Micropore diffusion controlled

- Mass transfer from bulk fluid to solid phase through fluid-particle interface
- Linear driving force assumed

Macropore diffusion controlled

- Mass transfer between bulk and pore fluid phases via external film on particle surface with concentration gradient
- Additional term: gas in pore

Sorbed Gas: SOL and POR models



Calculated mass transfer coefficient:

- 5% porosity: POR mass transfer coefficient = 480 * SOL
- 10% porosity: POR mass transfer coefficient = 250 * SOL

Future Work

- Measure high PT **sorption simultaneously with acoustic & resistivity**
- Quantify errors in the **approximation of average adsorbed gas** phase over wide range of pressure and temperature
- Extend theoretical model to better represent physical process in shales
  - combine macro- and micropore resistance to diffusion
  - use measured sorption data for shales
- Implement **multilayer adsorption** for macropores
- Compare permeability of CO_2, inert gas (N_2) and water in fractured shale
- Compile and compare permeability, acoustics, resistivity, and sorption data

Acknowledgements

Department of Energy, USA

Chesapeake Energy Company

- Manika Prasad, Sanyog Kumar, Yijia Zhang
- Bill Carey and Luke Frash
- Ronny Pini

APPENDIX

Milestones and Deliverables

Task	Milestone	Description	Completion Date		Deliverable
			Reported	Actual	
T1	M1	Kickoff Meeting with Co-PI's	11/6/2014	11/6/2014	Minutes of Meeting
T1	M1	Kickoff Meeting at NETL	11/12/2014	11/12/2014	Presentation
T6	M6.1	Sample Selection / Distribution	11/30/2014	11/30/2014	Minutes of Meeting
T2	M2.1.1	X-ray Tomographic Characterization of Samples Prior to Triaxial Experiments	5/31/2015	3/31/2015	Report & Presentation
T3	M3.1	Sample Characterization	9/30/2015		Report & Presentation
T3	M3.2.1	Protocol for High Pressure Equilibrium Adsorption Measurements	11/30/2015		Lab Manual
T4	M4.1.1	Analytical Methods to Assess High Pressure Dynamic Processes during Adsorption	11/30/2015	1/31/2016	Lab Manual
T5	M5.1	Acoustic and Attenuation Measurements at Various CO2 Pressures on Intact and Damaged Samples	1/31/2016	4/30/2016	Report & Presentation
T6	M6.1	Sample Selection / Distribution	11/30/2015		Minutes of Meeting

Gantt Chart

Gantt chart showing major milestones. The green color marks completed quarters

Task	BP1 - YEAR 1 Nov 2014-Sep 2015)				BP2 - YEAR 2 (Oct 2015 - Sep 2016)			YEAR 3 Oct 2016 - Sep 2017)		
	Q1	Q2	Q3	Q4	Q5	Q6	July-Oct	Nov-Feb	Mar-June	July-Oct
1.0	m1			m2	m3		m4	m5		m6
2.1				M2.1.1					M2.1.2	
2.2				M2.2.1			M2.2.2	M.2.2.3	M2.2.4	
2.3										M2.3
3.1				M3.1						
3.2					M3.2.1			M3.2.2		
3.3									M3.3	
4.1					M4.1.1			M4.1.2		
4.2									M4.2	
4.3							M4.3			
5.1					M5.1					
5.2							M5.2			
5.3								M5.3		
5.4									M.5.4	
6.0	M6.1				M6.2					M6.3

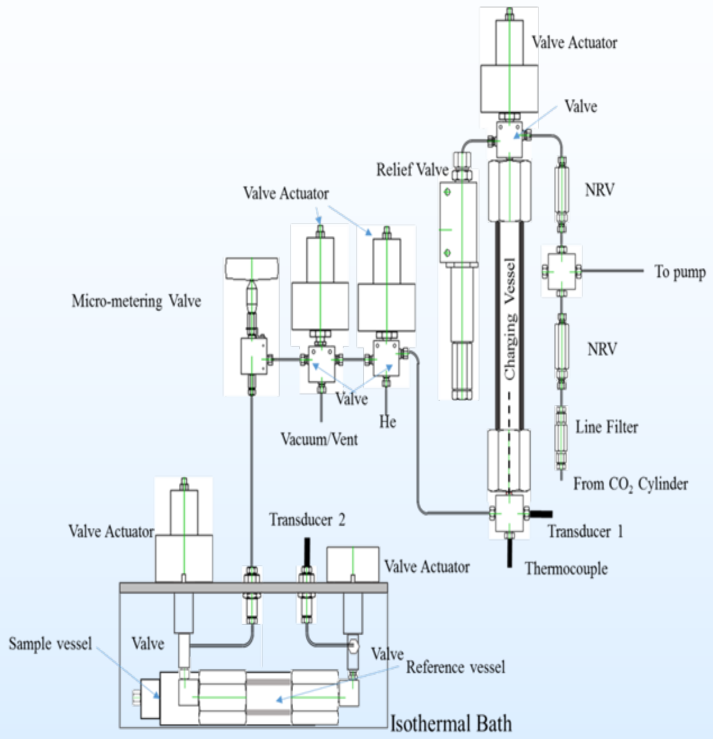
Bibliography

- Conference Paper:
  - Kumar, S., Prasad, M., Pini, R., Selective Adsorptives to Study Pore Structure and Wetting Behavior of Self-resourcing Shales: SPWLA, Long Beach (18-22nd July).
- Consortuim Presentations:
  - Kumar, S., Selective Adsorptives to Study Pore Structure and Wetting Behavior of Self-resourcing Shales: OCLASSH Research Consortium Meeting, Colorado School of Mines (16-17th June).
  - Zhang, Y., Error Analysis of Sorption System: OCLASSH Research Consortium Meeting, Colorado School of Mines (16-17th June).
  - Saleh, M., Experimental Setup and Measurement Protocol for Gas Sorption: OCLASSH Research Consortium Meeting, Colorado School of Mines (16-17th June).
  - Joewondo, N., Equation of state calculations for sorption in clay and organic-rich rocks: OCLASSH Research Consortium Meeting, Colorado School of Mines (16-17th June).

Free Space Protocol

Measurement Protocol:

1. Experiment starts with components at vacuum
2. Valve 6 opens
3. Valve 7 closed when transducer in the bath reads around a predetermined valve
4. Reading in P2 and T2 is allowed to equilibrate, it reads $P_{RV,1}$
5. Valve 7 opens
6. Gas in RV expands in SV as well as sorbs in the sample
7. New Pressure reading in transducer after equilibration is $P_{SV,1}$



Number of free molecules in the system before Valve 7 opens is given by $\boldsymbol{n_1} = \frac{p_{RV,1}V_{RV}}{z(P_{RV,1},T_{Iso})RT_{Iso}}$

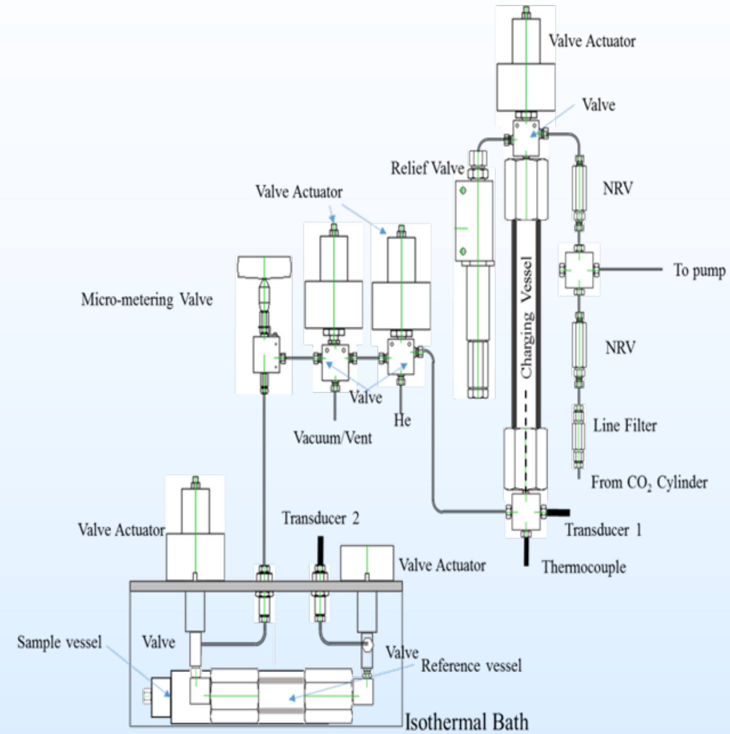
Number of free molecules in the system, after Valve 6 opens is given by $\boldsymbol{n_1'} = \frac{p_{SV,1}\{V_{RV}+V_{RV}\}}{z(P_{SV,1},T_{Iso})RT_{Iso}}$

Number of adsorbed molecules in the system is given by, $\boldsymbol{n_1^{ads}} = \boldsymbol{n_1} - \boldsymbol{n_1'}$

Adsorption Cycle Protocol

Measurement Protocol:

1. Experiment starts with components at vacuum
2. Valve 6 opens
3. Valve 7 closed when transducer in the bath reads around a predetermined valve
4. Reading in P2 and T2 is allowed to equilibrate, it reads $P_{RV,1}$
5. Valve 7 opens
6. Gas in RV expands in SV as well as sorbs in the sample
7. New Pressure reading in transducer after equilibration is $P_{SV,1}$



Number of free molecules in the system before Valve 7 opens is given by $\boldsymbol{n_1} = \frac{p_{RV,1} V_{RV}}{z_{(P_{RV,1}, T_{Iso})} R T_{Iso}}$

Number of free molecules in the system, after Valve 6 opens is given by $\boldsymbol{n_1'} = \frac{p_{SV,1}\{V_{RV} + V_{RV}\}}{z_{(P_{SV,1}, T_{Iso})} R T_{Iso}}$

Number of adsorbed molecules in the system is given by, $\boldsymbol{n_1^{ads}} = \boldsymbol{n_1} - \boldsymbol{n_1'}$

Desorption Cycle Protocol

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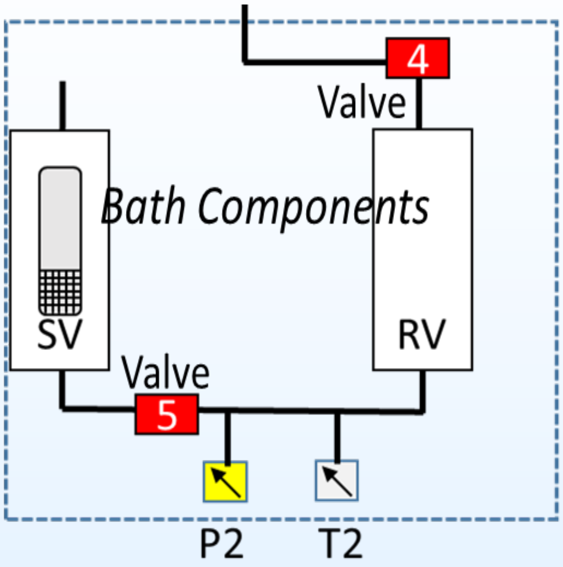
Adsorption Cycle: 1st Data Point

1. Experiment starts with components at Vacuum
2. Assume opening Valve 4 introduces RV with gas, pressure of which is read as $P^e_{RV,1}$ by the transducer



- Calculated free molecules in the system before Valve 5 opens:

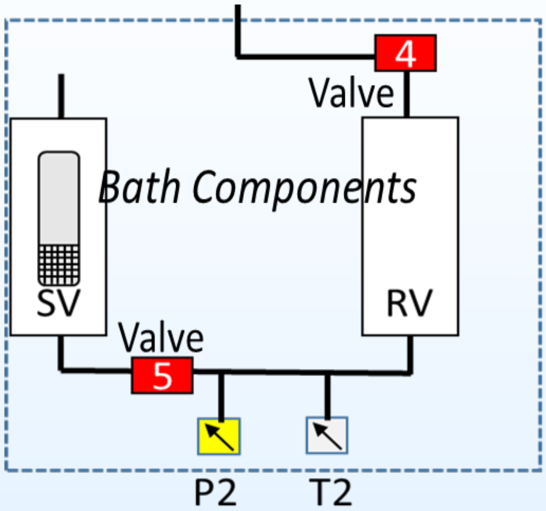
$$n^e_1 = \frac{P^e_{RV,1} V_{RV}}{Z_{(P_{RV,1}, T_{Iso})} R T_{Iso}}$$

From the known isotherm, ***Iterate*** the following to solve for the free molecule after Valve 5 opens, $n'^{,e}_1$ and reading in transducer $P^e_{SV,1}$:

$$\begin{cases} n'^{,e}_1 = n^e_1 - n^{ads}_1 \\ n'^{,e}_1 = \dfrac{P^e_{SV,1}\{V_{SV} + V_{RV}\}}{Z_{(P^e_{SV,1}, T_{Iso})} R T_{Iso}} \\ n^{ads}_1 = \dfrac{V_{max} b \, P^e_{SV,1}}{1 + b \, P^e_{SV,1}} \end{cases}$$

Adsorption Cycle: 2nd Data Point

1. Experiment starts with Valve 5 closed



- Calculated free molecules in the system before Valve 5 opens: $$n_2^e = \frac{P_{RV,1}^e V_{RV}}{Z_{(P_{RV,1},T_{Iso})} R T_{Iso}} + n_1^{\prime,e}$$

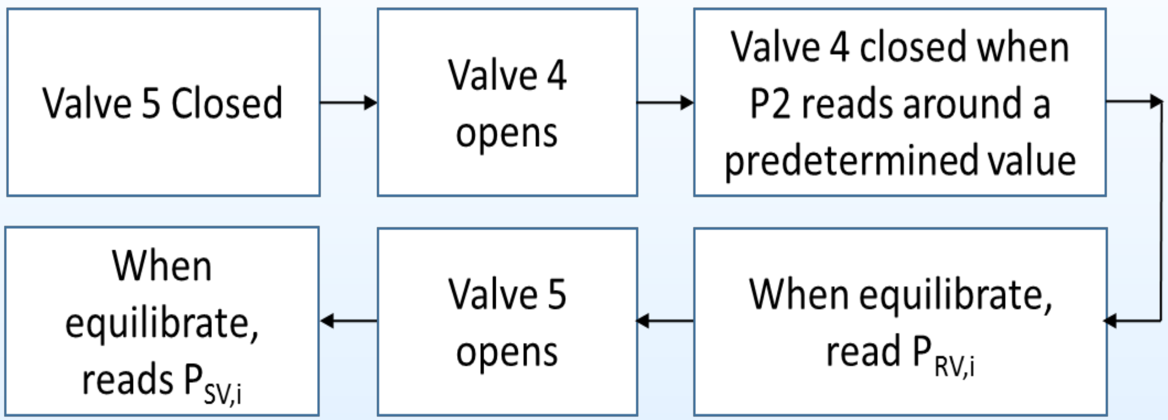
From the known isotherm, ***Iterate*** the following to solve for the free molecule after Valve 5 opens, $n_1^{\prime,e}$ and reading in transducer $P_{SV,2}^e$:

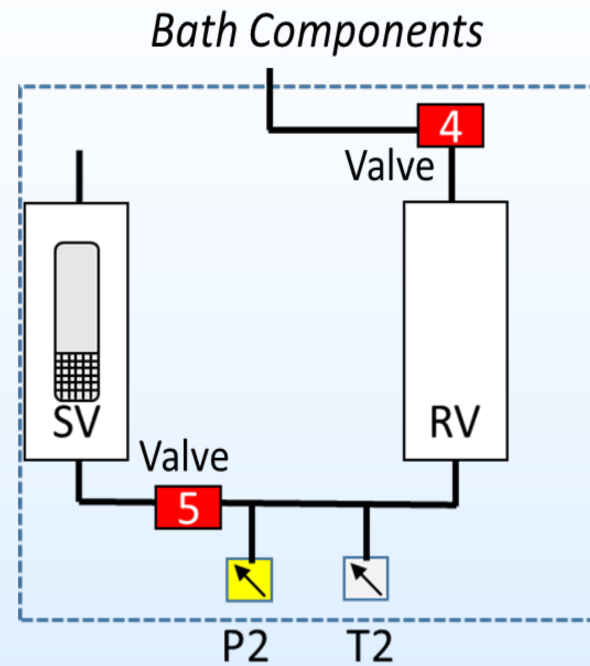
$$n_2^{\prime,e} = n_2^e - n_2^{ads} - n_1^{ads}$$

$$n_2^{\prime,e} = \frac{P_{SV,2}^e \{V_{SV} + V_{RV}\}}{Z_{P_{SV,2}^e,T_{Iso})} R T_{Iso}}$$

$$n_1^{ads} = \frac{V_{max} b\, P_{SV,2}^e}{1 + b\, P_{SV,2}^e}$$

Adsorption Cycle: i^{th} Data Point





Number of free molecules in the system before Valve 5 opens:

$$n_i = \frac{P_{RV,i} V_{RV}}{Z_{(P_{RV,i},T_{Iso})} R T_{Iso}} + n_{i-1}^{ads}$$

Number of free molecules in the system, after Valve 5 opens:

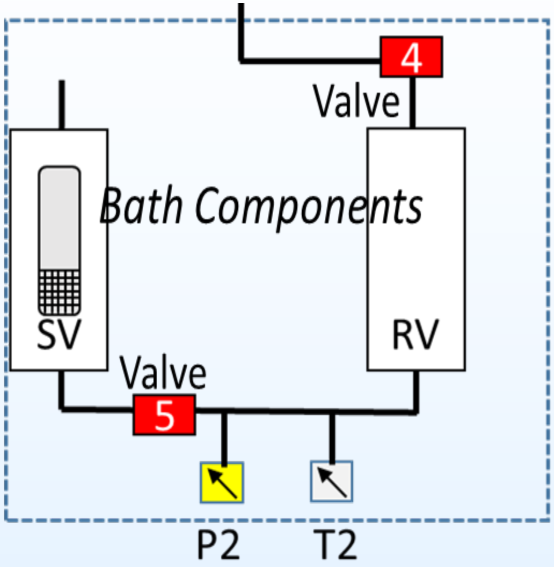
$$n_i' = \frac{P_{SV,i}\{V_{SV} + V_{RV}\}}{Z_{(P_{SV,i},T_{Iso})} R T_{Iso}}$$

Number of adsorbed molecules in the system:

$$n_i^{ads} = n_i - n_i' + n_{i-1}^{ads}$$

Erroneous Transducer Reading

- Modify the assumed pressure $\left(P^{e}_{RV,i}\right)$ and calculated pressure $\left(P^{e}_{SV,i}\right)$ values using the known transducer accuracy ($\pm Error\,\% = \pm$e)



- Calculated free molecules in the system before valve 5 opens:

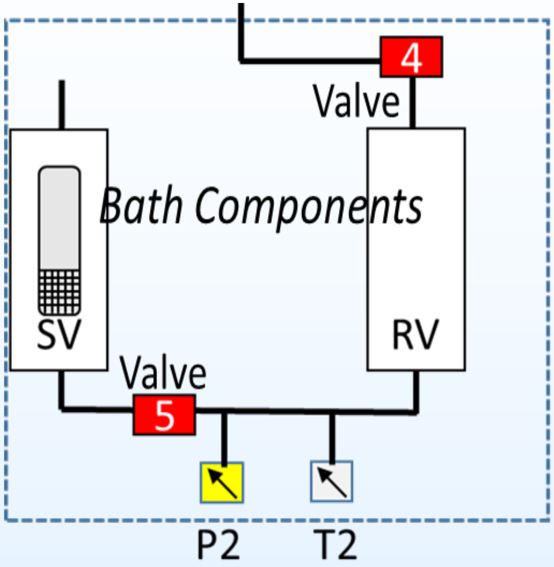
$$n_2^e = \frac{P^e_{RV,1}(1 \pm \mathrm{e}/100)V_{RV}}{Z_{(P_{RV,1},T_{Iso})}RT_{Iso}} + n_1^{\prime,e}$$

From the known isotherm, ***Iterate*** the following to solve for the free molecule after Valve 5 opens, $n_1^{\prime,e}$ and reading in transducer $P^e_{SV,2}$:

$$\begin{cases} n_2^{\prime,e} = n_2^e - n_2^{ads} - n_1^{ads} \\ n_2^{\prime,e} = \dfrac{P^e_{SV,2}(1 \pm \mathrm{e}/100)\{V_{SV} + V_{RV}\}}{Z_{(P^e_{SV,2},T_{Iso})}RT_{Iso}} \\ n_1^{ads} = \dfrac{V_{max}b\, P^e_{SV,2}(1 \pm \mathrm{e}/100)}{1 + b\, P^e_{SV,2}(1 \pm \mathrm{e}/100)} \end{cases}$$

Erroneous Transducer Reading

- Modify the assumed pressure $\left(P^{e}_{RV,i}\right)$ and calculated pressure $\left(P^{e}_{SV,i}\right)$ values using the known transducer accuracy ($\pm Error\,\% = \pm$e)



- Calculated free molecules in the system before valve 5 opens:

$$n^{e}_{2} = \frac{P^{e}_{RV,1}(1 \pm \mathrm{e}/100)V_{RV}}{Z_{(P_{RV,1},T_{Iso})}RT_{Iso}} + n^{\prime,e}_{1}$$

From the known isotherm, ***Iterate*** the following to solve for the free molecule after Valve 5 opens, $n^{\prime,e}_{1}$ and reading in transducer $P^{e}_{SV,2}$:

$$\begin{cases} n^{\prime,e}_{2} = n^{e}_{2} - n^{ads}_{2} - n^{ads}_{1} \\ n^{\prime,e}_{2} = \dfrac{P^{e}_{SV,2}(1 \pm \mathrm{e}/100)\{V_{SV}+V_{RV}\}}{Z_{(P^{e}_{SV,2},T_{Iso})}RT_{Iso}} \\ n^{ads}_{1} = \dfrac{V_{max}b\,P^{e}_{SV,2}(1 \pm \mathrm{e}/100)}{1 + b\,P^{e}_{SV,2}(1 \pm \mathrm{e}/100)} \end{cases}$$

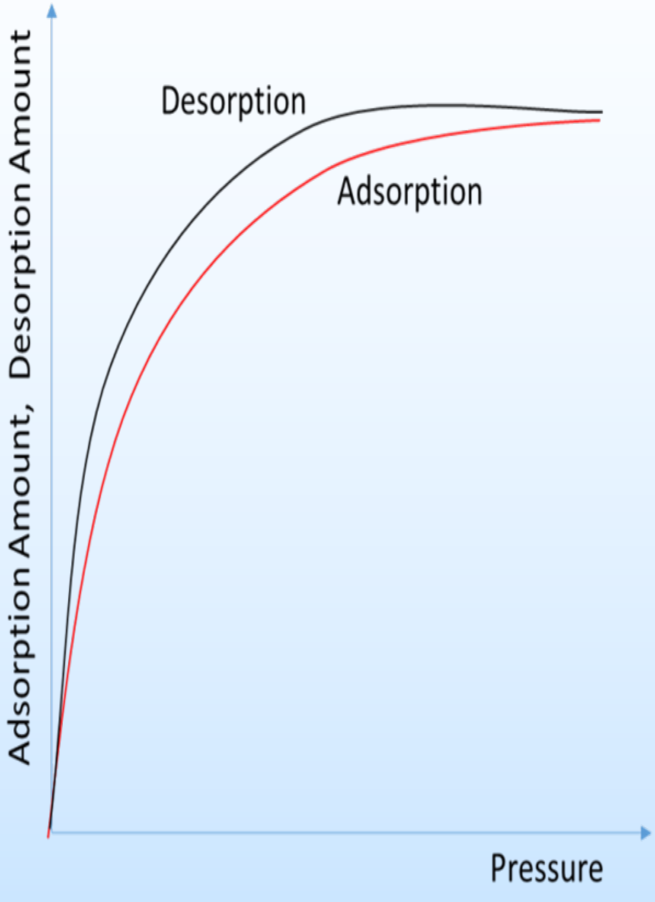
Adsorption Isotherm Construction

Error Analysis Motivation:

- Obtain most accurate pressure readings
- Determine minimum accuracy needed for the pressure transducers
- Optimize amount of sample

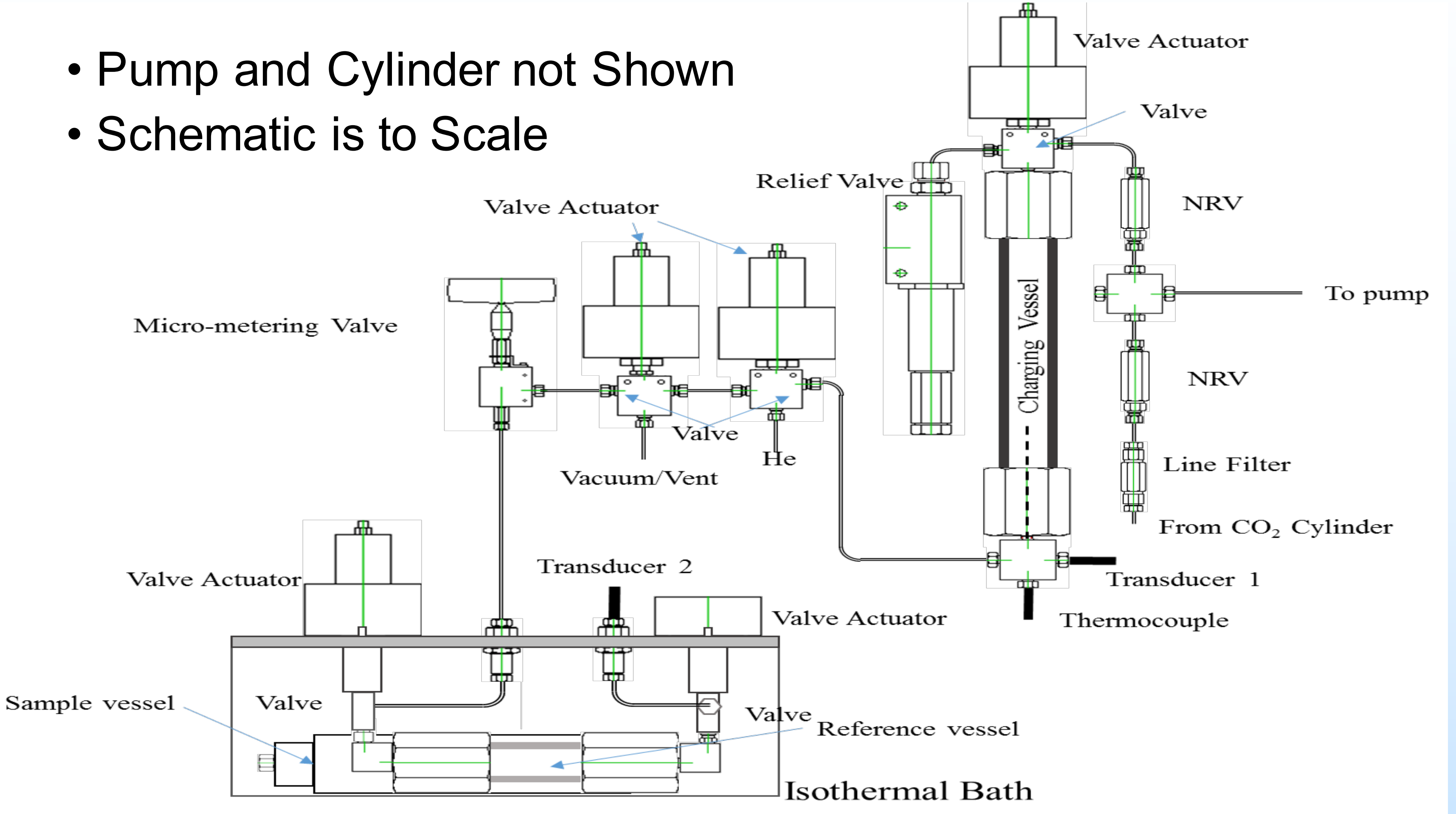
Pressure	Adsorption Cycle, Adsorption amount
$P_{sv,1}$	n_1^{ads}
$P_{sv,2}$	n_2^{ads}
$P_{sv,i}$	n_i^{ads}
.	.
.	.

Pressure	Desorption Cycle, Adsorption amount
$P_{sv,1}$	n_1^{des}
$P_{sv,2}$	n_2^{des}
$P_{sv,i}$	n_i^{des}
.	.
.	.



A Closer Look

- Pump and Cylinder not Shown
- Schematic is to Scale



End of Presentation

Equations of State

SOL

$$c_{0_{SOL}}(V_c - V_s) + q_0 V_s = c(V_c - V_s) + \bar{q} V_s$$

$$\frac{dc}{dt} = -\frac{d\bar{q}}{dt}\frac{V_s}{V_c - V_s}$$

$$\frac{d\bar{q}}{dt} = k_M(q_E - \bar{q})$$

$$q_E = f(c); langmuir$$

POR

$$c_{0_{POR}}(V_c - V_B) + c_{0_p} V_p + \; q_0 V_s = c(V_c - V_B) + \overline{c_p} V_p + \bar{q} V_s$$

$$\frac{dc}{dt} = -\frac{\left(\frac{d\bar{q}}{dt}V_s + \frac{d\overline{c_p}}{dt}V_p\right)}{V_c - V_B}$$

$$\frac{d\bar{q}}{dt}V_s + \frac{d\overline{c_p}}{dt}V_p = k_M(c - \overline{c_p})V_p$$

$$q = f(c_p); langmuir$$

Improve equations presentation