Impact of Carbonate Mineral Dissolution on Hydrocarbon Transport in Shales

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Outline

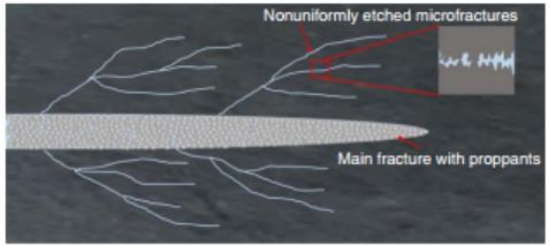
- Introduce the problem
- What has been done: Literature Review
- Areas to Tackle
- Necessary tools: Theory and Lab Practices
- Preliminary Work
- Conclusions and Future Course of Action

Courtesy of Guenther Glatz

CO2 Potential on Carbonates-Rich Shales?

- Gas potential: Marcellus, Barnett, and Haynesville alone ~ 2500 TCF (DOE/NETL 2009)
  - 20-30% recovery
- Oil potential: 4.9 MMBbl/d in 2015 about 52% US oil production (EIA, 2017)
  - 5-10% recovery

- Reason:



(Wu and Sharma, 2015)

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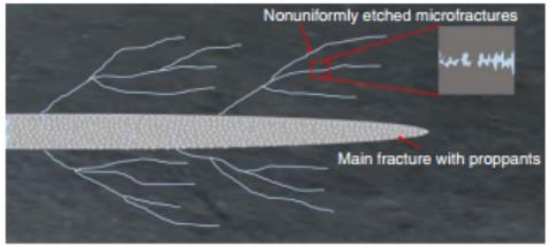
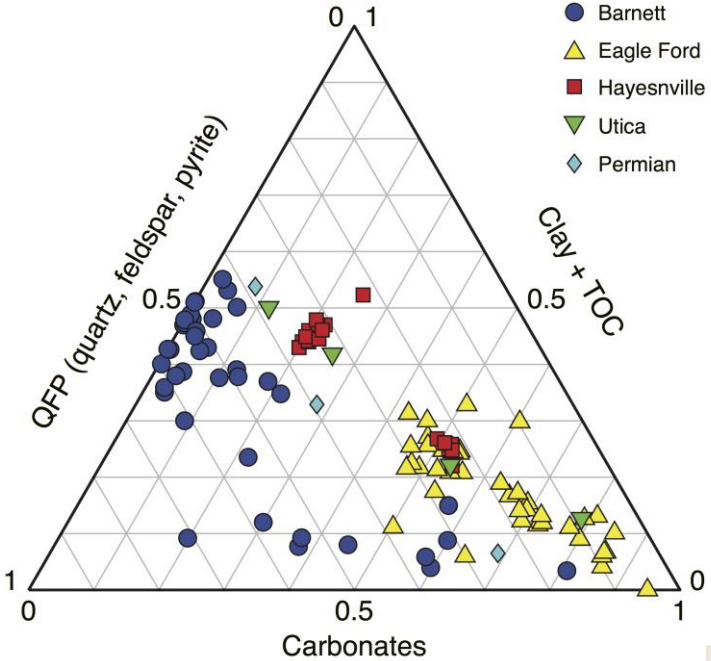


(Wu and Sharma, 2015)

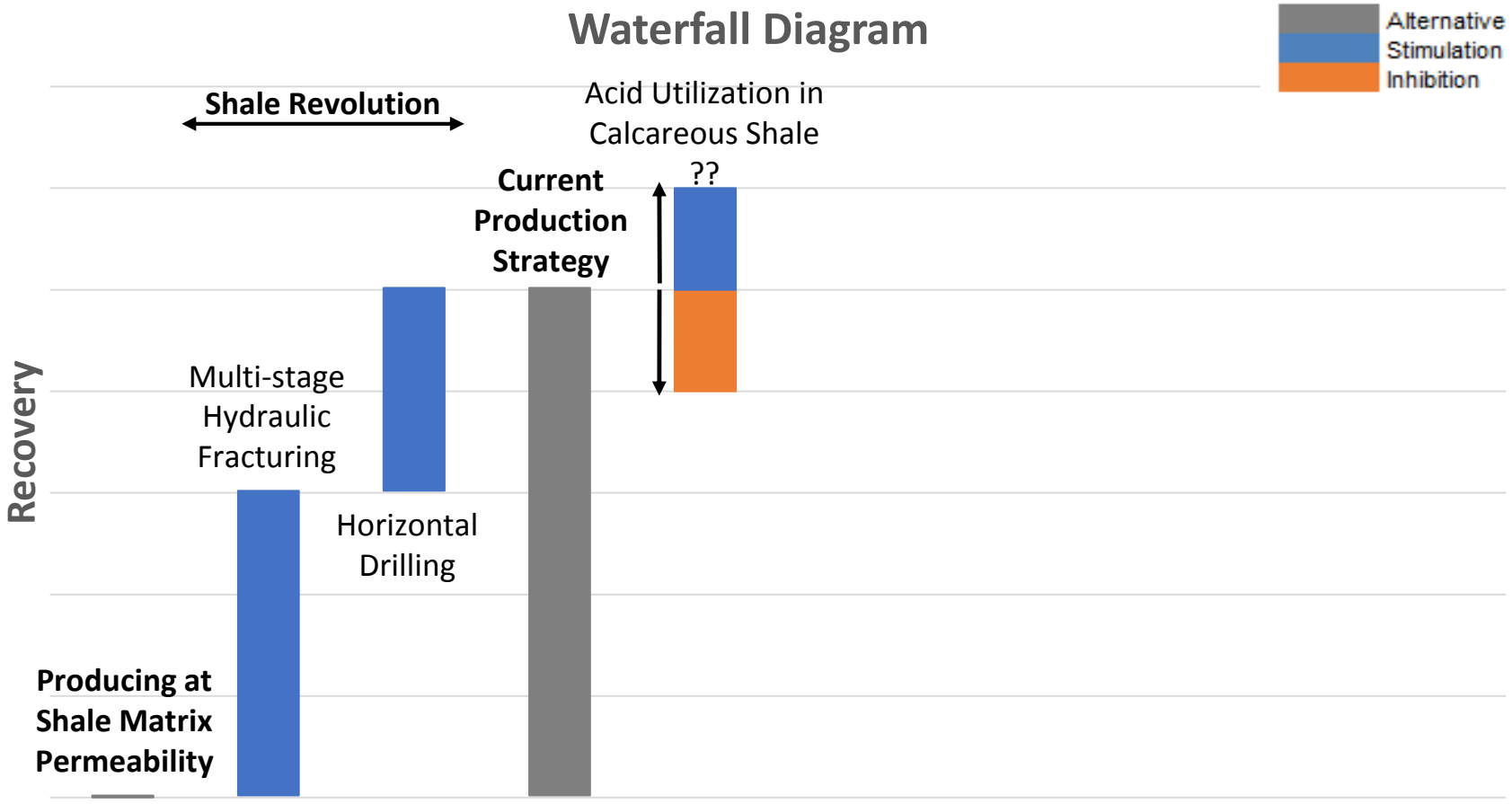
- Room for improvement:
  - pH of water in scCO2: 2.80 – 2.95

(Toews et al., 1995)



(Kohli, Unpublished)

Current Literature (1/2)



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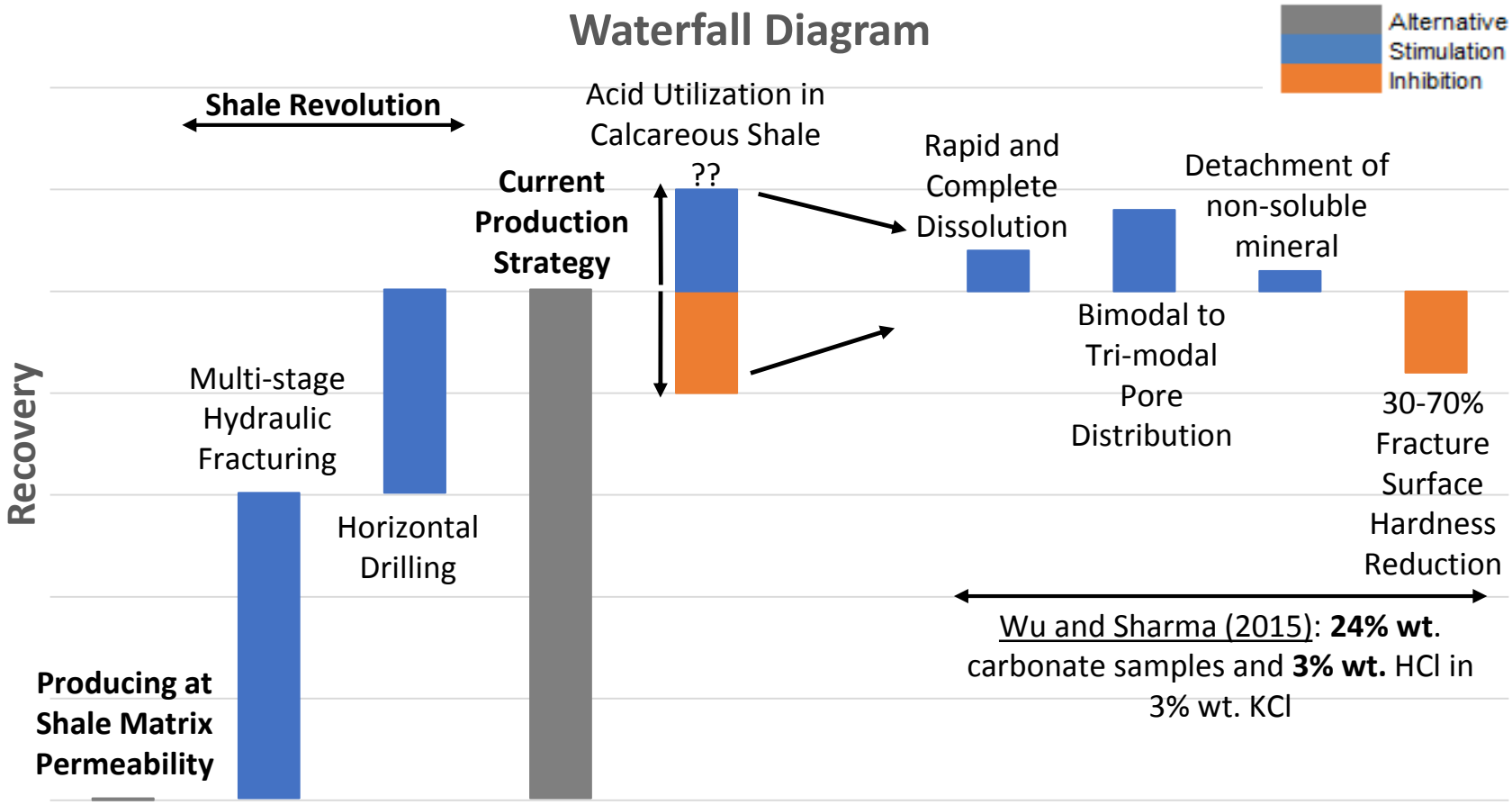
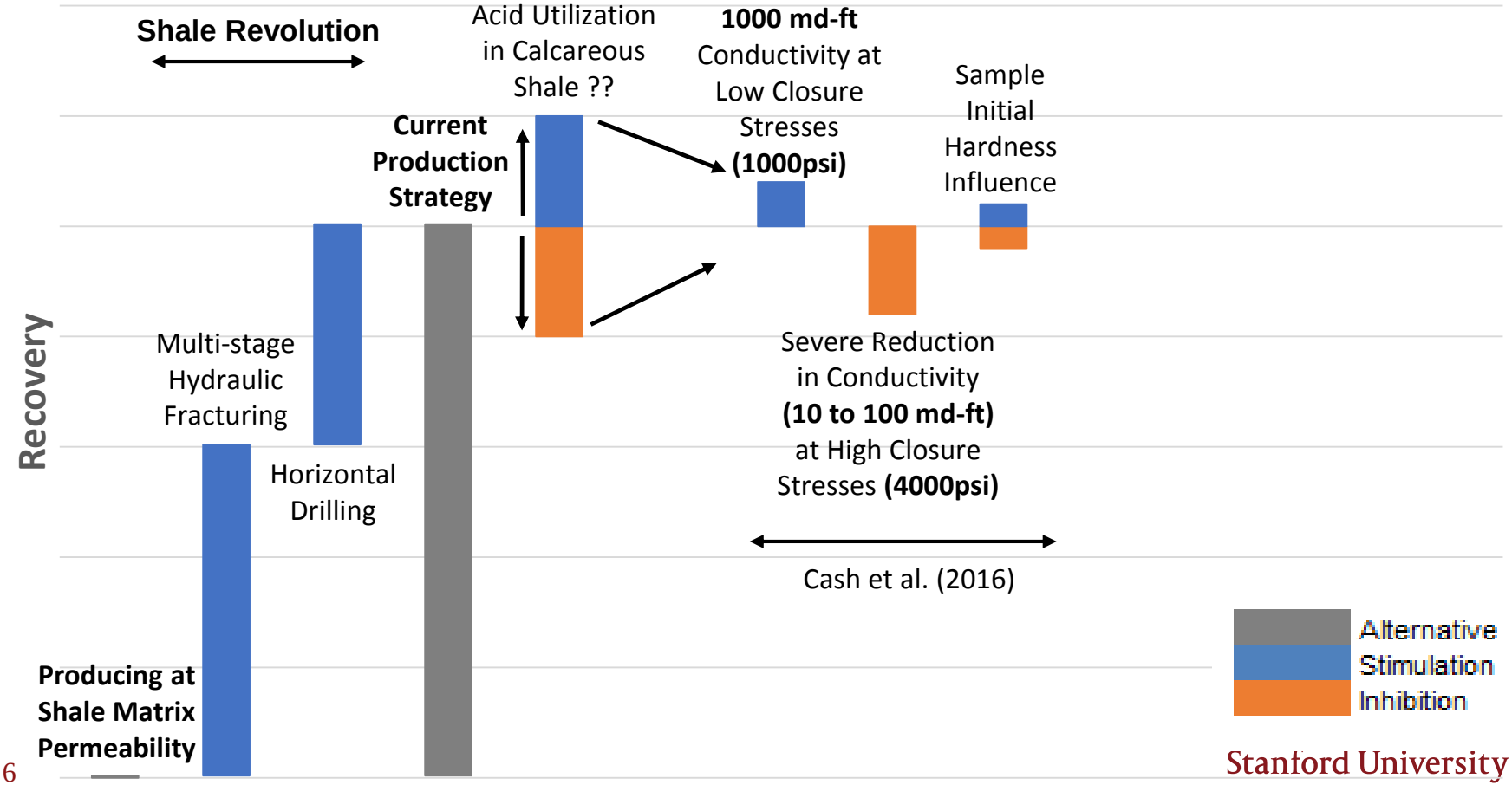


Current Literature (2/2)

Waterfall Diagram



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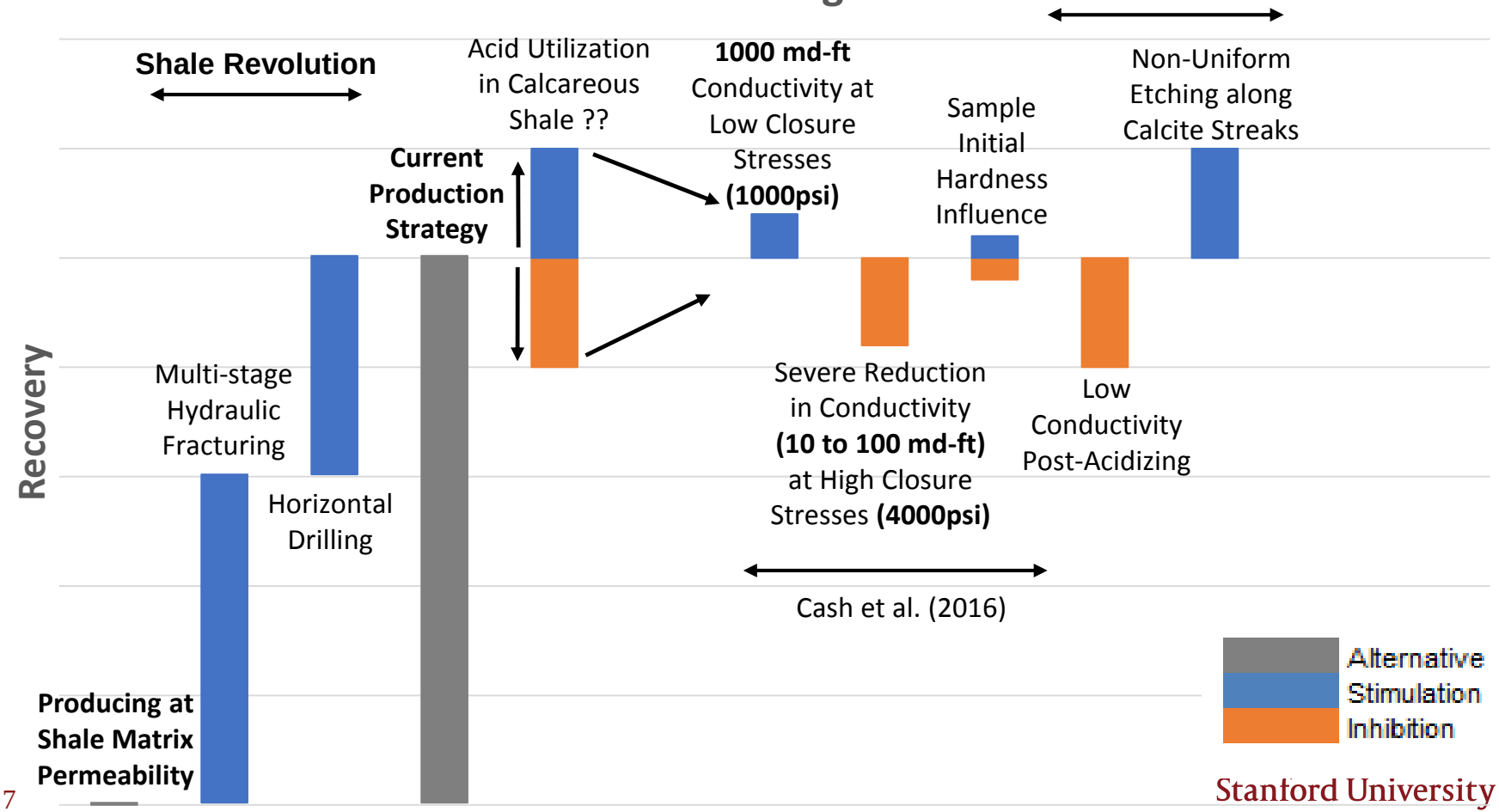

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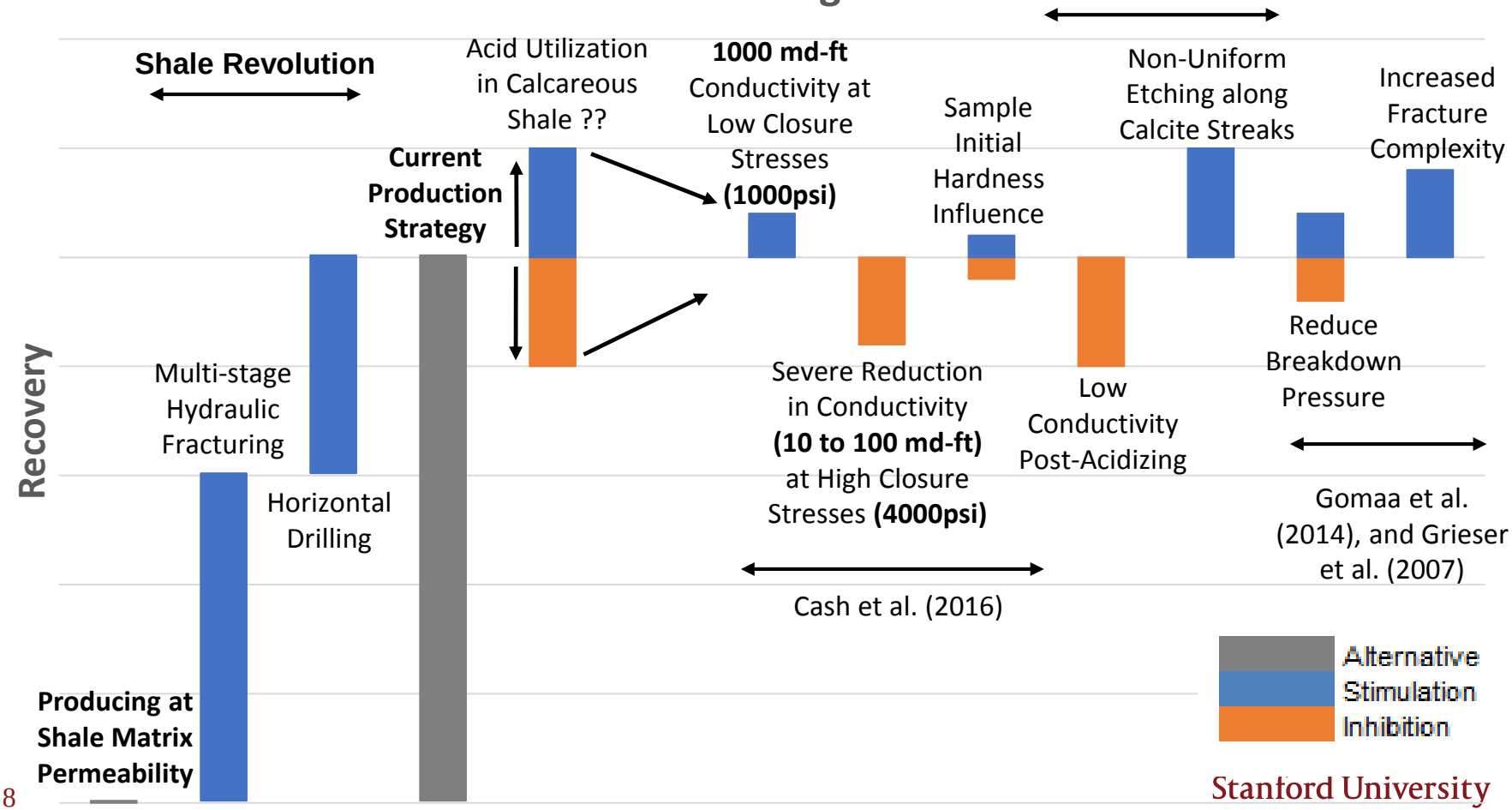
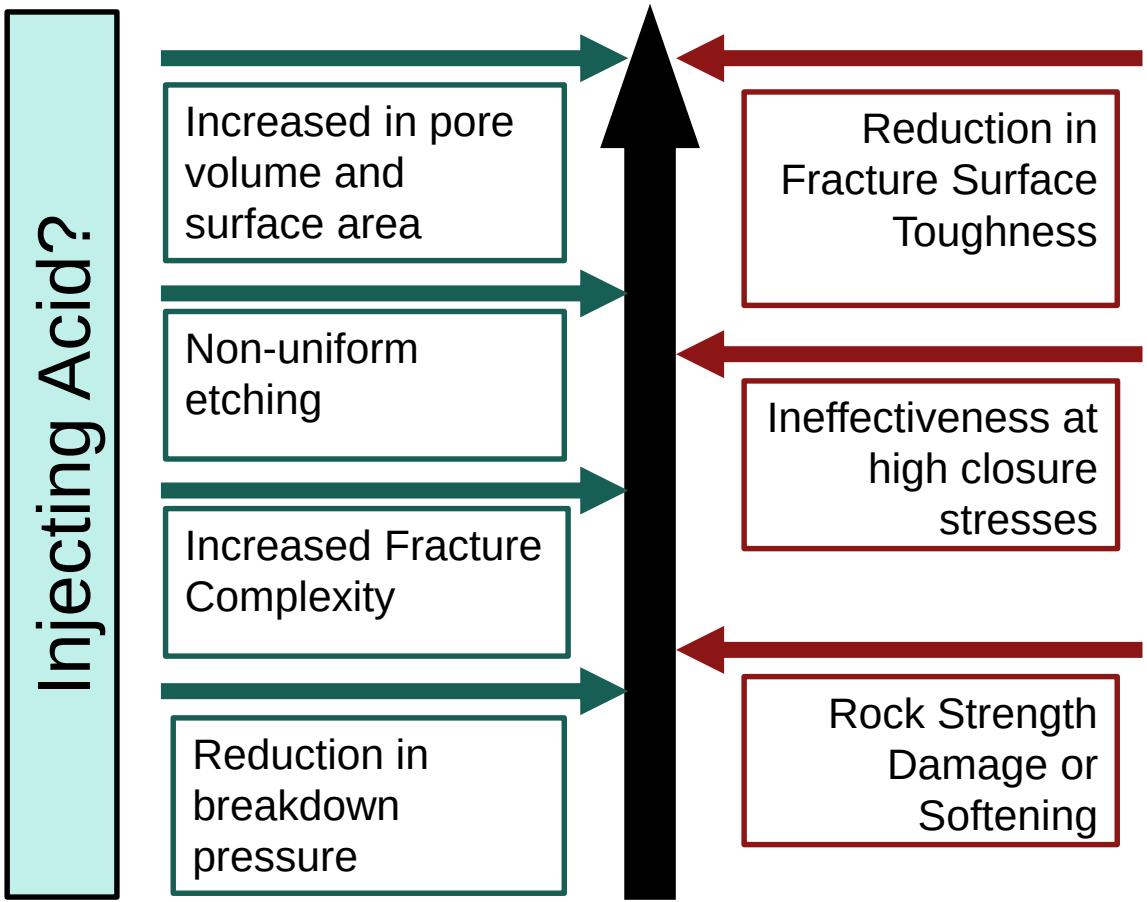


Summarizing



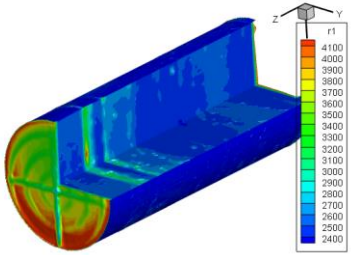
Theory (1/4)

CT Imaging

$$\frac{I}{I_0} = exp^{-\mu h}$$

$$CT = 1000\,\frac{\mu - \mu_w}{\mu_w}$$

$$\emptyset = \frac{CT_{kr} - CT_{ar}}{CT_k - CT_a}$$



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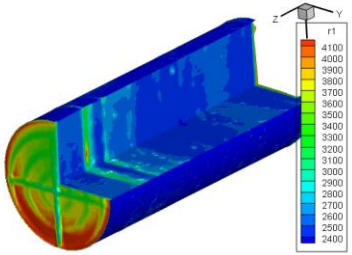

Pulse Decay

$$P_1 - P_f = \Delta P\left[\frac{V_2}{V_1} + V_2\right]e^{-\alpha t}$$

<u>Adsorption Influence</u>

$$\emptyset_a = \frac{\rho_s}{V_{std}}\,\frac{1-\emptyset}{c_g\rho}\,\frac{q_L p_L}{(p_L + p)^2}$$

$$k = \frac{s_1 \mu L c_g}{f_1 A\left(\frac{1}{V_u} + \frac{1}{V_d}\right)}$$

<u>Klinkenberg Correction</u>

$$k_a = k_{inf}\left(1 + \frac{K_b}{P}\right)$$

Theory (3/4)

CT Imaging

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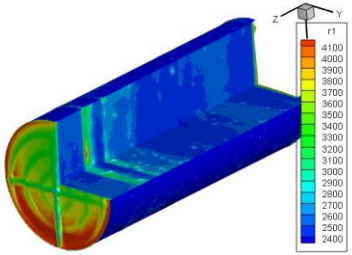

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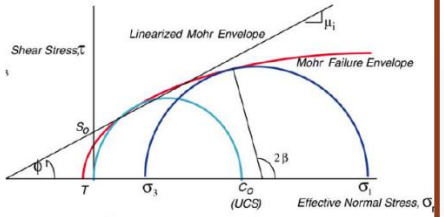
Rock Mechanics

$$E = \frac{F/A}{\Delta l / l_0}$$



Weak rock have weak cohesion

$$C_o = 2S_o\left[\left(\mu_i^2 + 1\right)^{1/2} + \mu_i\right]$$

Theory (4/4)

CT Imaging

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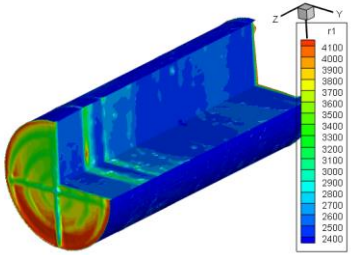

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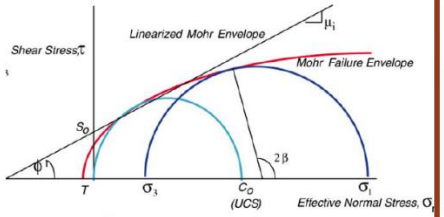

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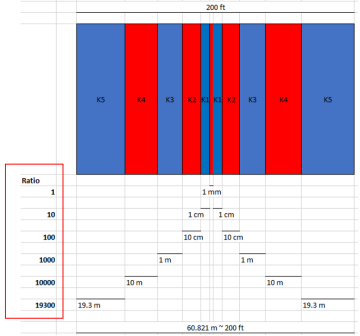
Well Testing (Simulation)

E300 Black Oil Compositional 2D Model

<u>Gridding Scheme</u>



$$s = \frac{k_e k_r h}{141.2 q B \mu}\Delta P_s$$

Preliminary Work

- Built core holder and designed experimental setup for pulse decay, krypton/CO2 injection, and CT scanning

- Conducted shale porosity and permeability measurements (characterization stage) and their evolution with increasing net effective stress

- Investigated potential high storage capacity zones using 3D Computed Tomography (CT) imaging and Quantitative X-Ray Diffraction (QXRD) mineralogical analysis

Experimental Workflow - Sample Preparation (1/3)

Vacuum Oven ~ 1-2 weeks

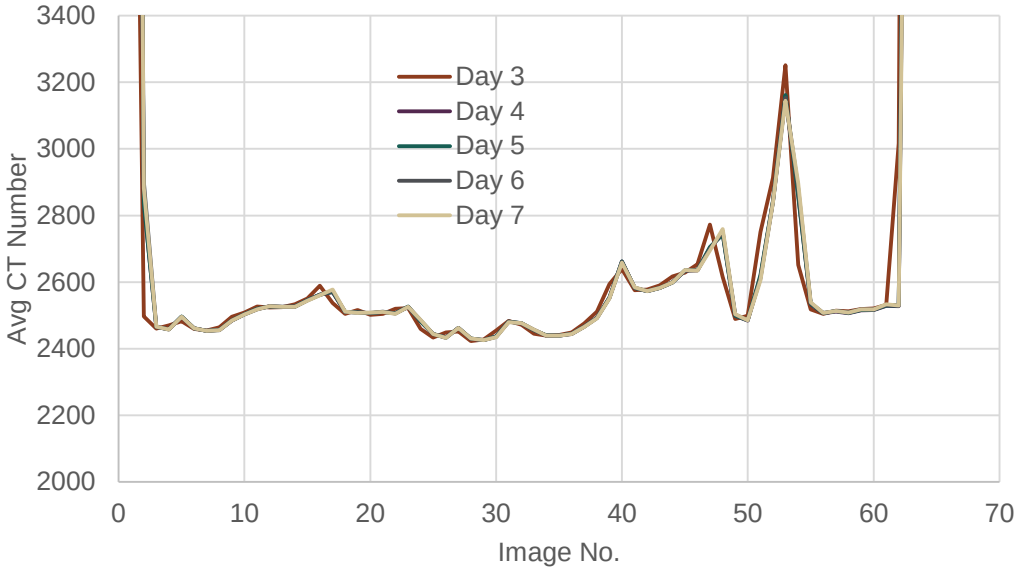
PTFE sleeve and aluminum foil

Experimental Workflow – Sample Preparation (1/3)

Sample Preparation

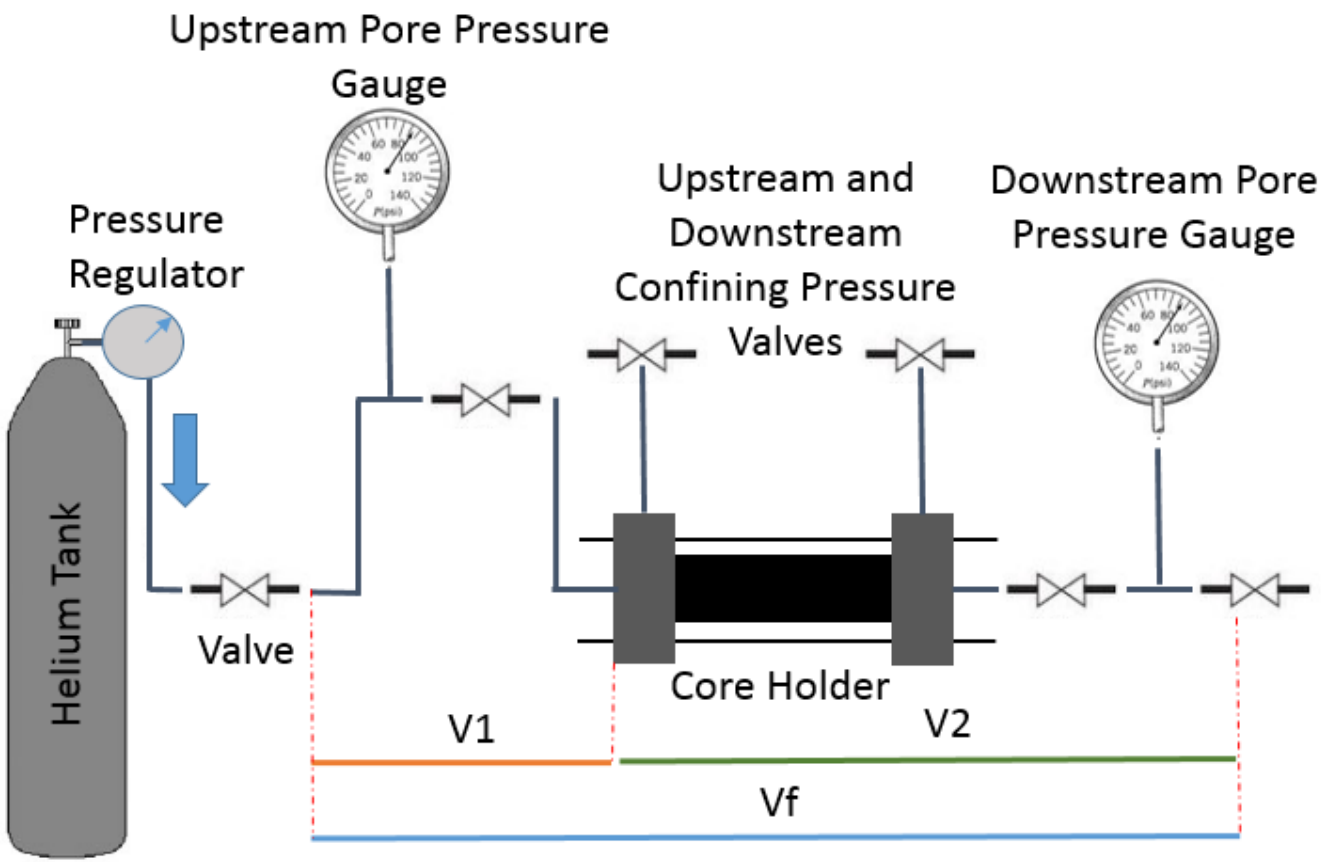
Experimental Workflow - Sample Preparation (1/3)

Sample Preparation



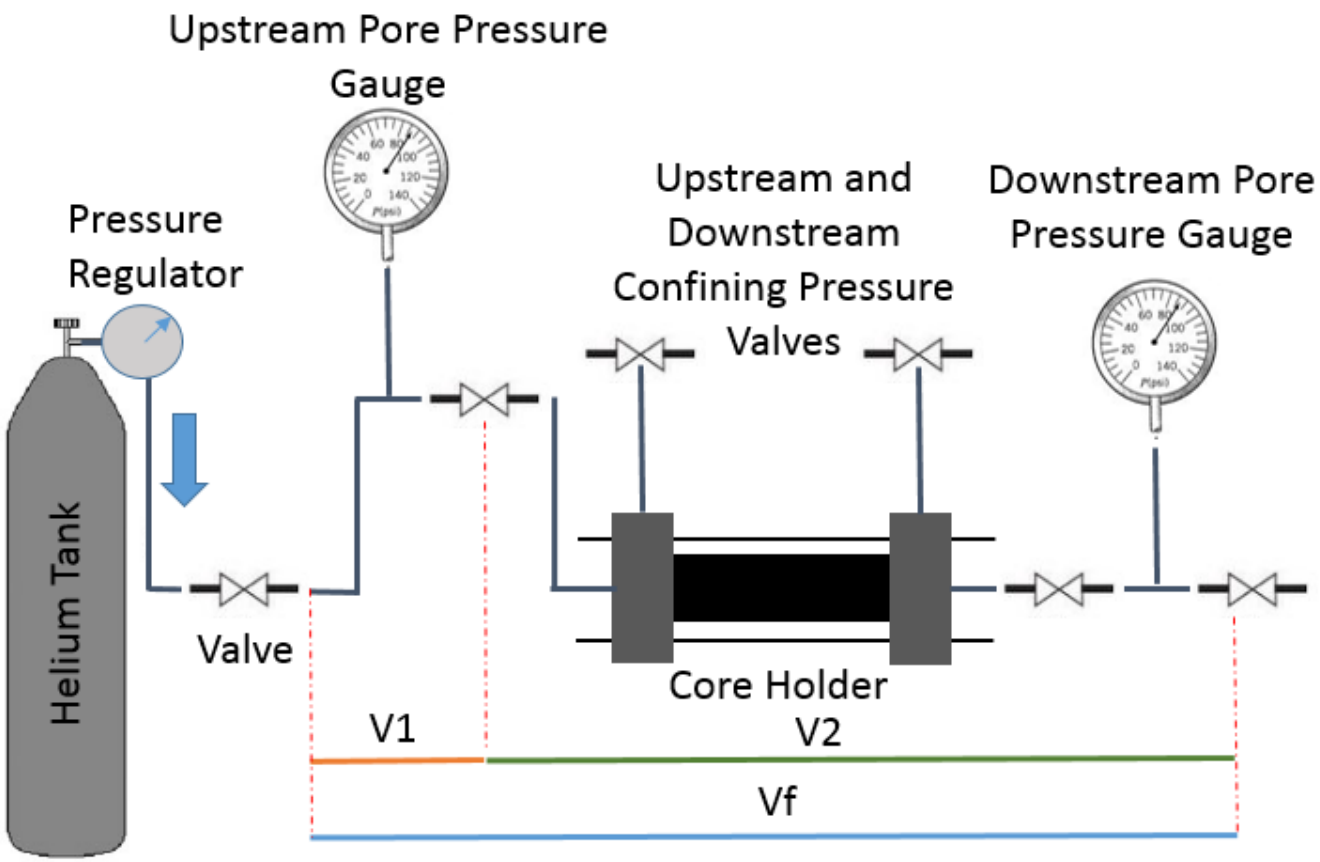
Vacuum under CT scanner

Experimental Workflow – Pulse Decay (2/3)



Pulse Decay Setup - Permeability

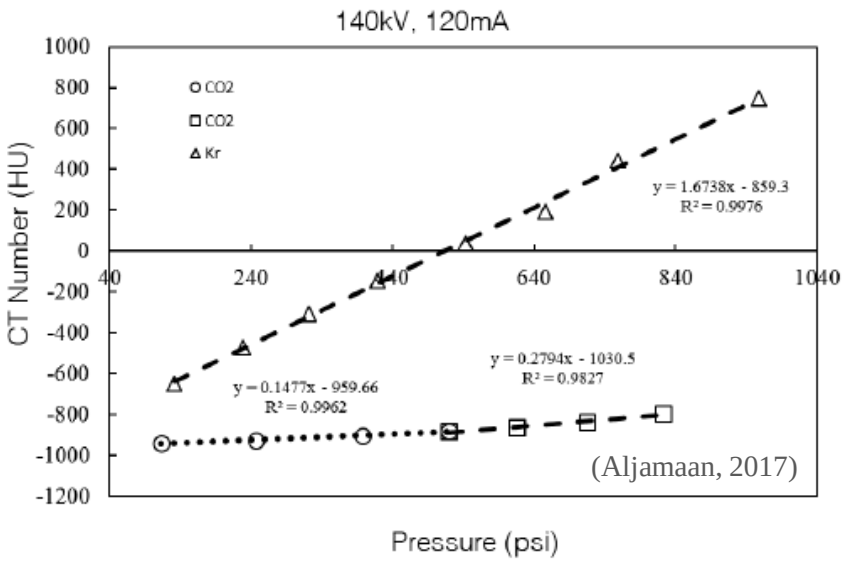
Experimental Workflow – Pulse Decay (2/3)



Pulse Decay Setup - Porosity

Experimental Workflow – Storage & CT Imaging (3/3)

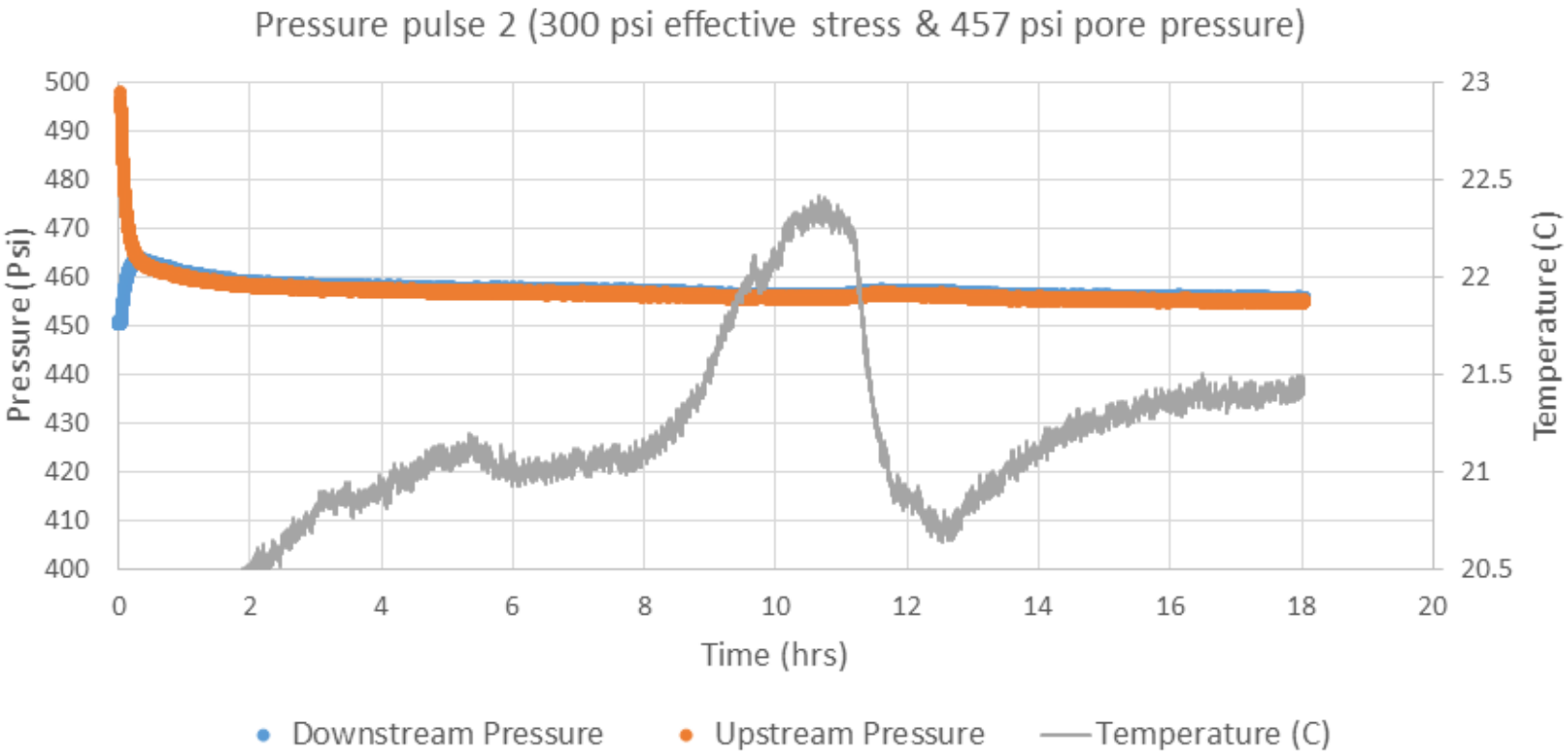
- Inject Krypton for porosity/storage capacity
- Wait for pressure equilibrium



(Aljamaan, 2017)

$$\emptyset = \frac{CT_{Krr} - CT_{ar}}{CT_{Kr} - CT_{a}}$$

Experimental Results: Pulse Decay Permeability



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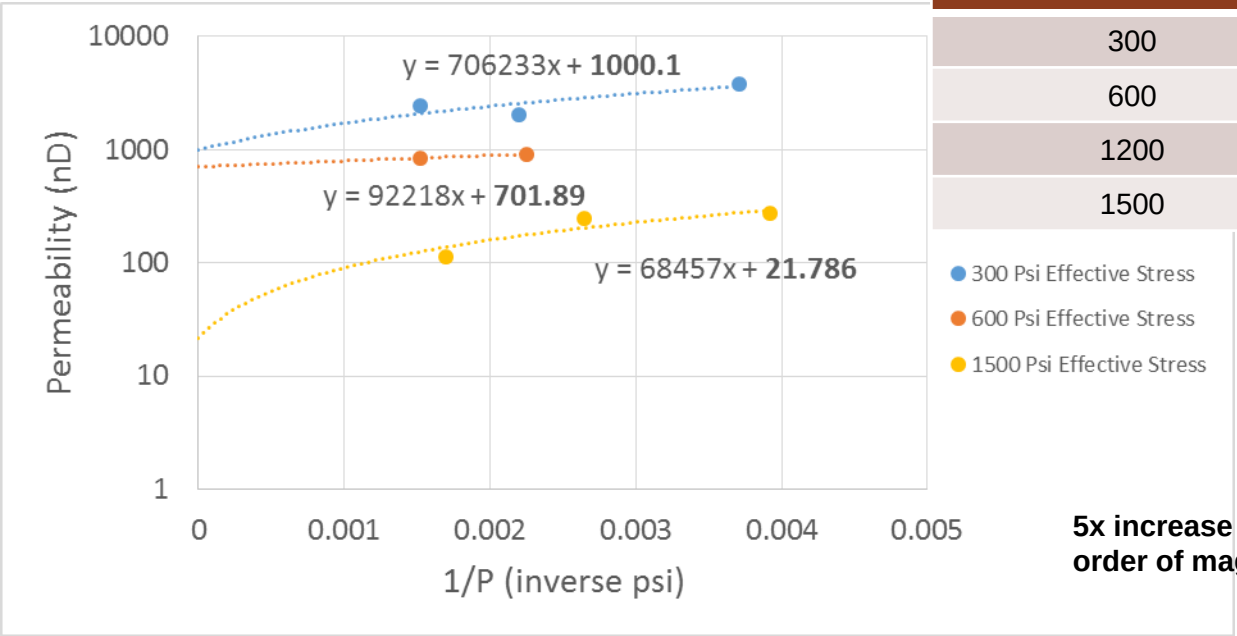


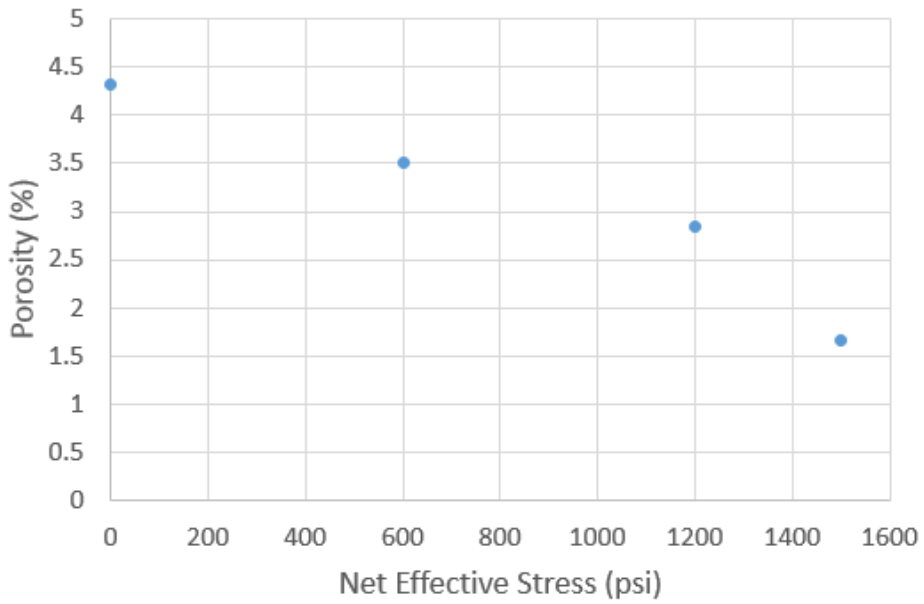
Effective Stress (Psi)	Liquid-like vertical permeability (nD)
300	1000
600	700
1200	N/A
1500	20

5x increase in effective stress resulted in ~1.5 order of magnitude reduction in permeability

Experimental Results: Pulse Decay Porosity

Effective Stress (Psi)	Porosity (%)	Avg. Equilibrium Time (hrs)
0	4.3*	N/A
600	3.5	12
1200	2.8	11
1500	1.7	21

*zero effective stress porosity calculated from mineral composition and grain density of averaged QXRD mineralogy data from 1ft interval above and below zone from which our sample was cored



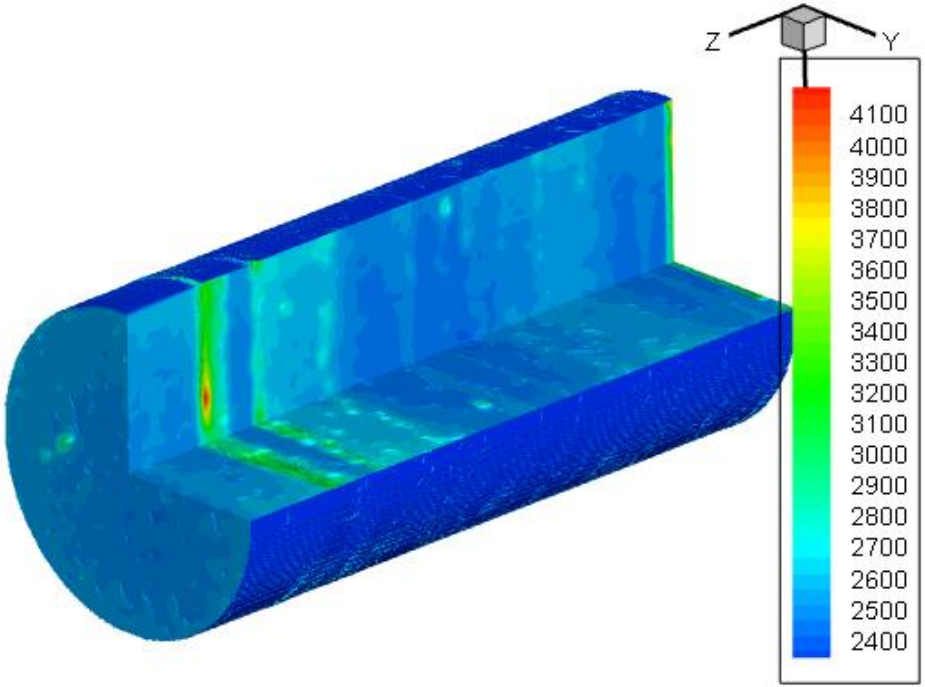
Mineral	Weight Percent	Density (g/cc)
Illite and smectite	18	2.79
Quartz	13	2.65
Plagioclase	2	2.67
Calcite	59	2.73
Ankerite or Excess Ca/Fe dolomite	4	2.87
Chlorite and pyrite	1	3.05
Organic matter	3	1.3
Grain Density	100	2.70

$$\emptyset = 1 - \frac{\rho_B}{\rho_g} = 1 - \frac{2.58}{2.695} = 0.043$$

Increasing effective stress to 1500 Psi results in a ~2.5 multiple reduction in porosity

Experimental Results: QXRD and 3D CT Image

Mineralogy	%
Pyrite	1-2
Chlorite	0-1
Ankerite or Excess Calcium Dolomite	4-5
Calcite	50-60
Clay	20
Quartz	13



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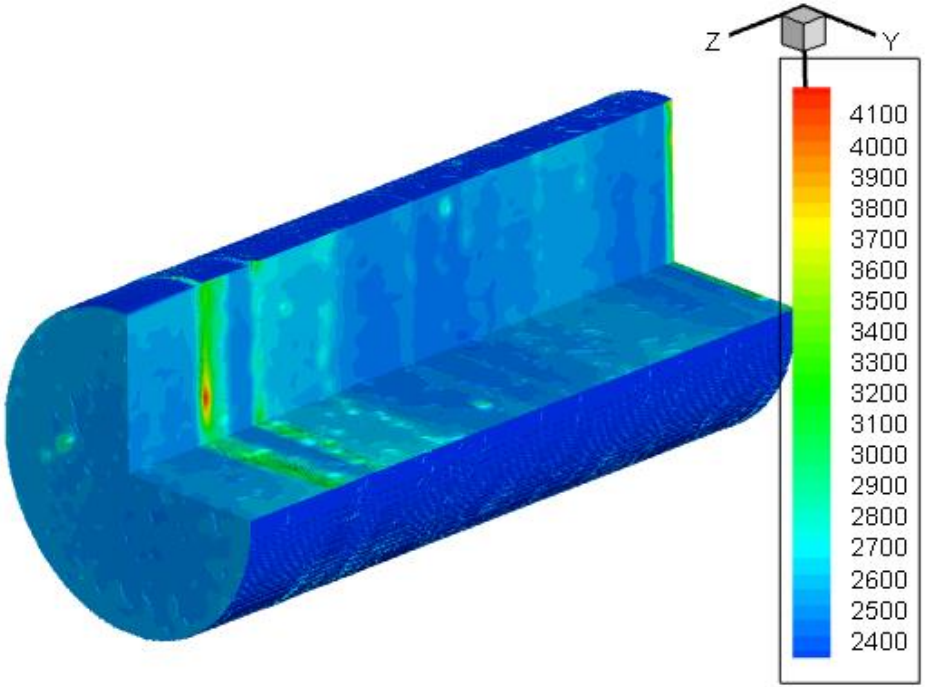
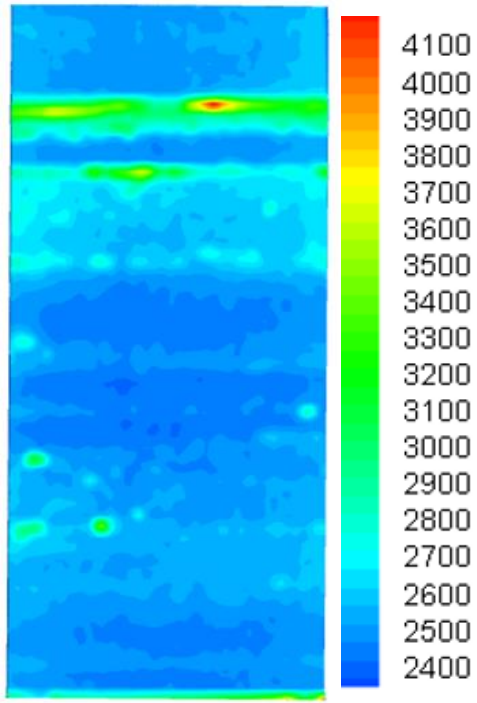
Mineralogy	Color
Pyrite	red
Ankerite or Excess Calcium Dolomite	green
Calcite	light blue
Clay and Quartz	dark blue

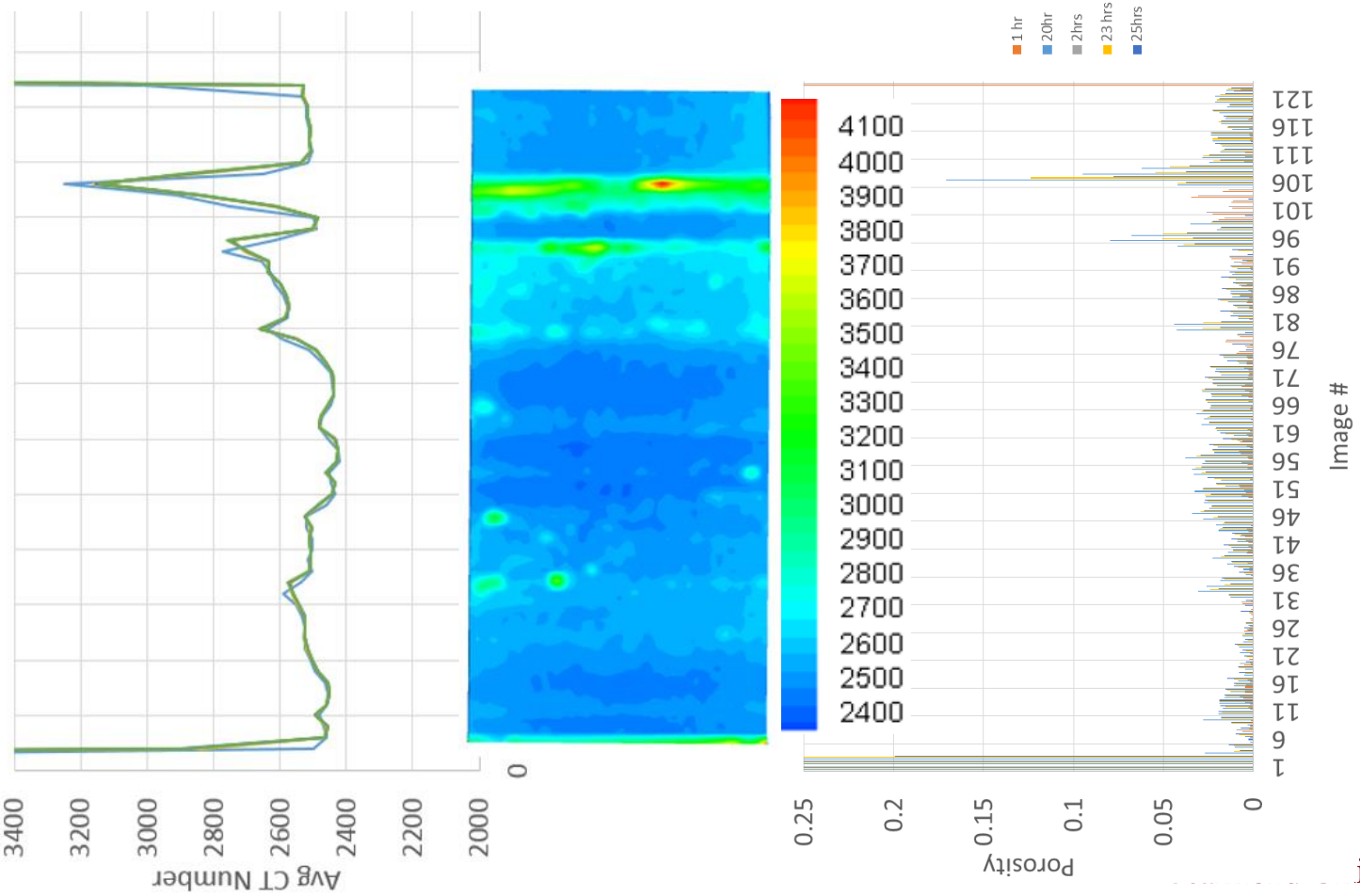


Experimental Results: 2-D Storage Capacity Zones



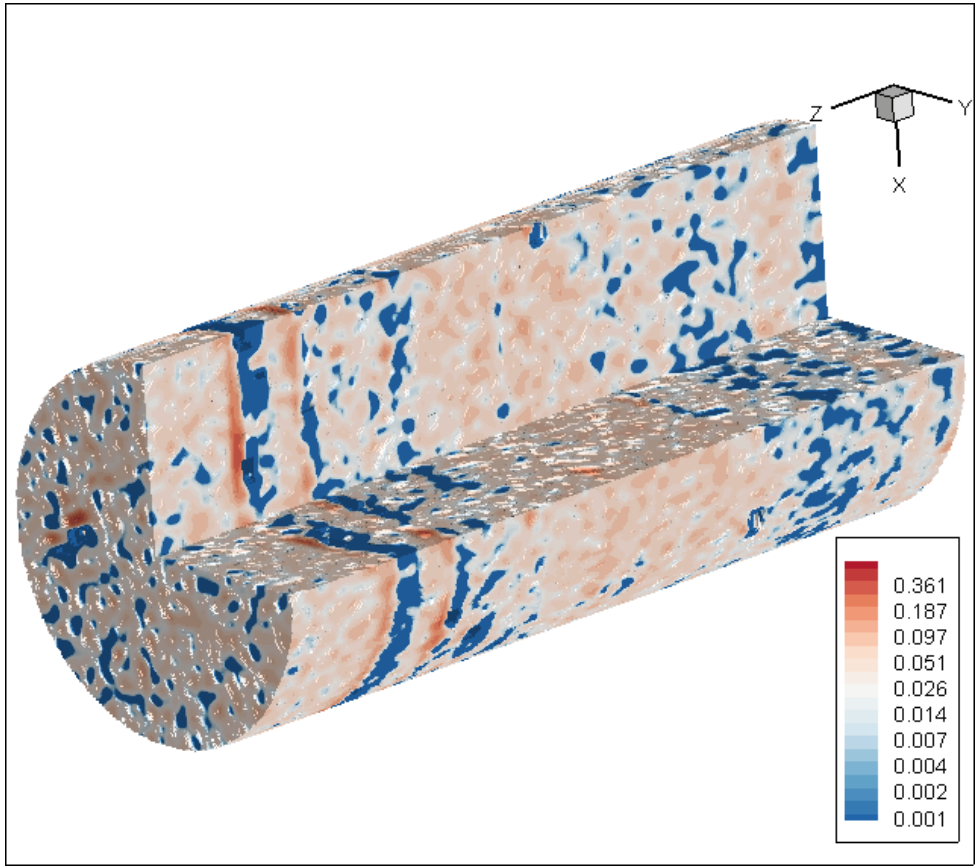
2-D Slice

Experimental Results: 2-D Storage Capacity Zones



Experimental Results: 3-D Storage Capacity Construction

- Exponential Color Scale
  - Displays 3 different porosity scales
    - 10-30% near Ankerite-rich zones
    - 1-10% in most of sample
    - <1% possibly in high Quartz regions
- Krypton storage capacity = 3.9%
  - Within experimental error from helium's at 300psi effective stress
  - Adsorption could account for additional capacity observed



Conclusion

- Workflow established for characterizing permeability, porosity, and mineralogy

- Pulse Decay:
  - Severe matrix permeability reduction (1000nD to 20nD) at high effective stress
  - 2.5 multiple reduction in porosity (4.3% to 1.7%) at high effective stress
  - Independent QXRD derived porosity in agreement with pulse decay trend

- QXRD and CT Imaging:
  - Location of different carbonates and high density minerals within W2 sample

- Krypton Storage Capacity Study:
  - Associates high storage zones with high carbonate zones
  - Storage capacity of 3.9%, similar to helium porosimetry results from pulse decay experiment

Future Work

- Use triaxial setup to measure Young's modulus and fracture sample

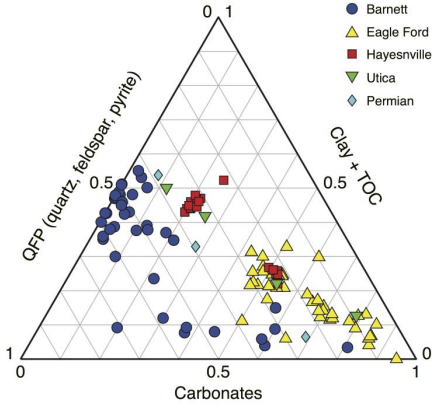
Courtesy of Guenther Glatz

- Saturate fractured core with crude oil

- Inject supercritical CO2 then introduce water (create acid) to assess enhanced recovery using mass balance and CT imaging techniques

Acknowledgements

- Tony
- Elliot and Shale group: Hamza, Beibei, and Bolivia
- Arjun Kohli and Guenther Glatz
- SUPRI-A members
- SUPRI-A affiliates for financial support



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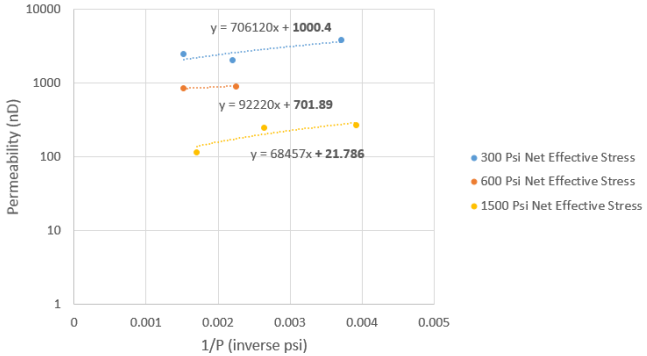
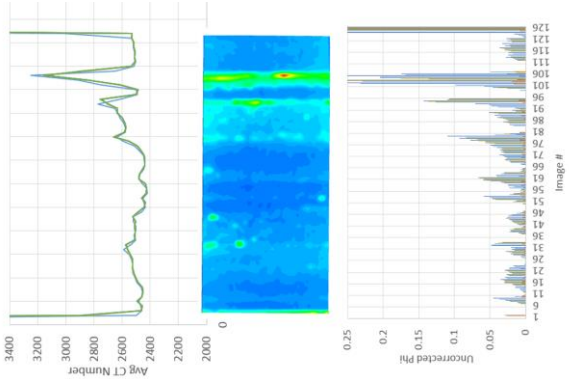
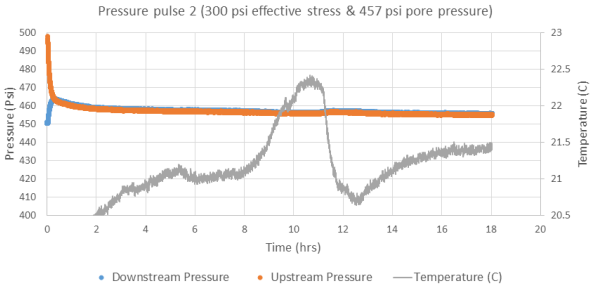
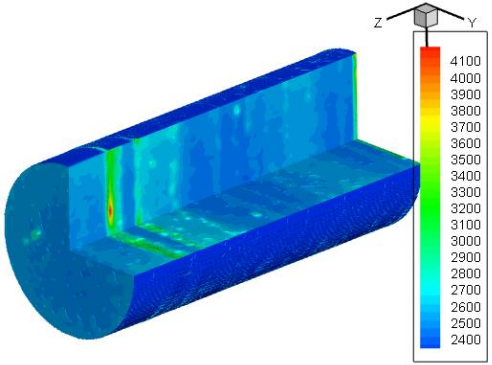


Thank You!



Question?

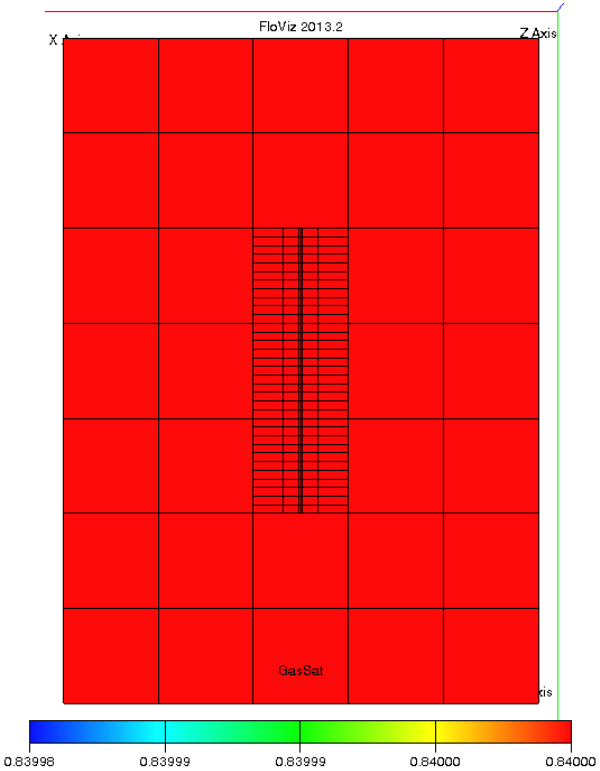




Appendix

Simulation Work & Problem Framing

Simulation Work (Grid)



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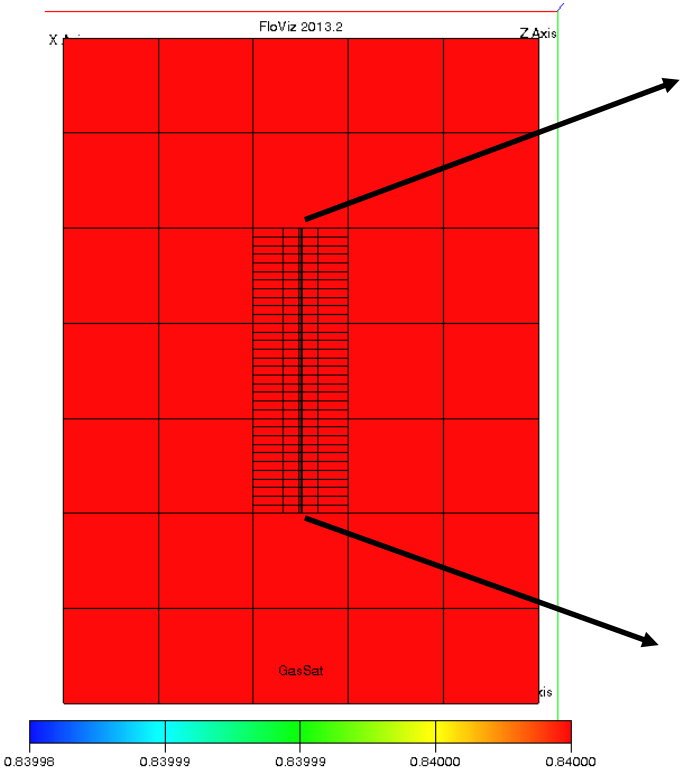
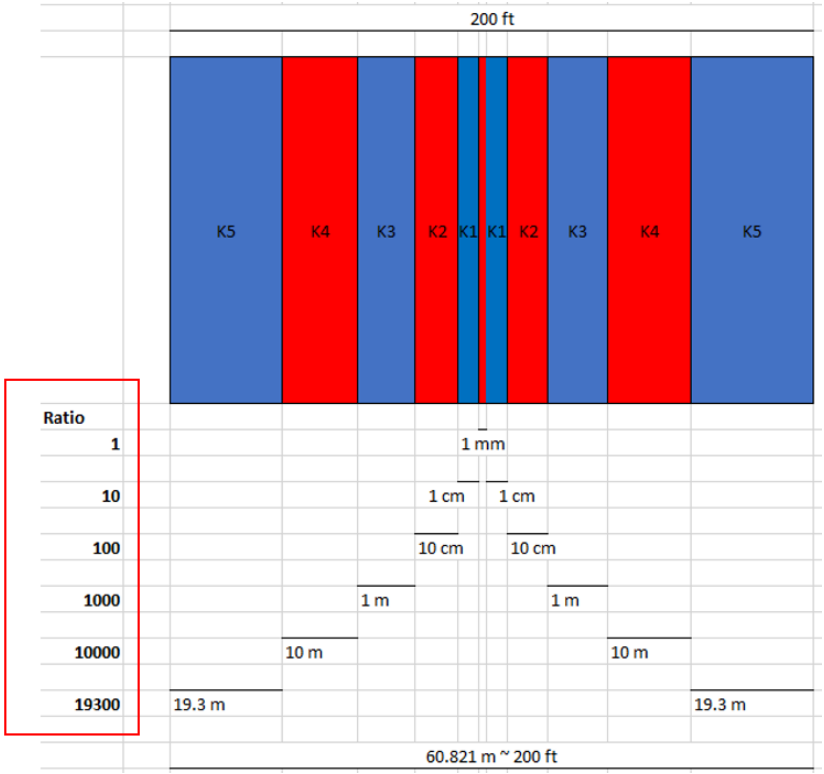
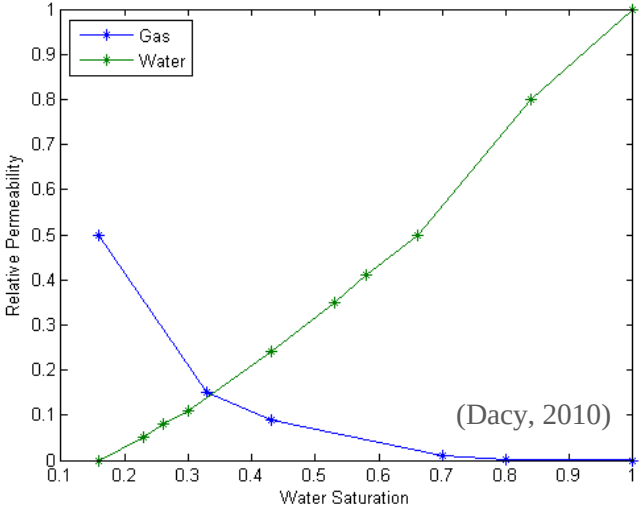
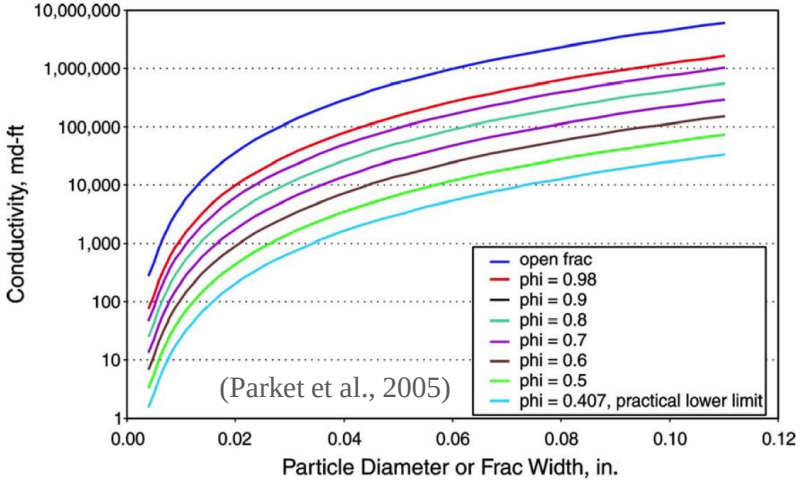




Simulation Work (Fluid and Rock Properties)





Ge and Ghassemi et al., (2012) estimated stimulation going up to 200 times the original matrix permeability in Barnett samples. Assumed x100 and logarithmic decrease in permeability away from fracture until matrix permeability.

Simulation Work (Results)

Parameter	Value	Units
q	0.1	$MSCF/D$
B	0.66	ft^3/SCF
μ	0.029	cp
h	100	ft
K_r	0.5	$--$
k	11.2	nD
ΔP_s	case dependent	psi

$$s = \frac{k_e k_r h}{141.2 q B \mu} \Delta P_s$$

Skin Values using common log gridding				
		Stimulated Distance Away from Fracture (cm)		
		2	22	222
Fracture Aperture (mm)	1	-4.11	-4.11	-4.11
	1.5	-4.12	-4.12	-4.12
	2.5	-4.12	-4.12	-4.12

Simulation Work – Grid Sensitivity Study (Results)

Skin Values using common log gridding				
		Stimulated Distance Away from Fracture (cm)		
		2	22	222
Fracture Aperture (mm)	1	-4.08	-4.08	-4.08
	1.5	-4.08	-4.08	-4.08
	2.5	-4.08	-4.10	-4.10

Skin Values using common log gridding				
		Stimulated Distance Away from Fracture (cm)		
		2	22	222
Fracture Aperture (mm)	1	-4.09	-4.09	-4.09
	1.5	-4.09	-4.09	-4.09
	2.5	-4.10	-4.10	-4.10

The different gridding schemes show no influence on skin results up to 1m away from the fracture surface on each end and for all reasonable fracture apertures

Framing the Problem

Acid as Fracing Fluid?	Acid Concentration?	Acid after Fracing?	Acid with Proppant?

Decisions

Framing… (2/3)

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Acid as Fracing Fluid?

Acid Concentration?

Acid after Fracing?

Acid with Proppant?

Decisions

Research Uncertainties

- Fracture Surface Softening
- Insoluble Mineral Detach
- Wettability Alteration
- Rock Strength
- Closure Stress Influence
- Gas Desorption / Diffusivity Rate

Practical Uncertainties

- Cost of Reactive Fluid
- Transportation
- Well Integrity
- Compatibility with Proppant

Framing… (3/3)

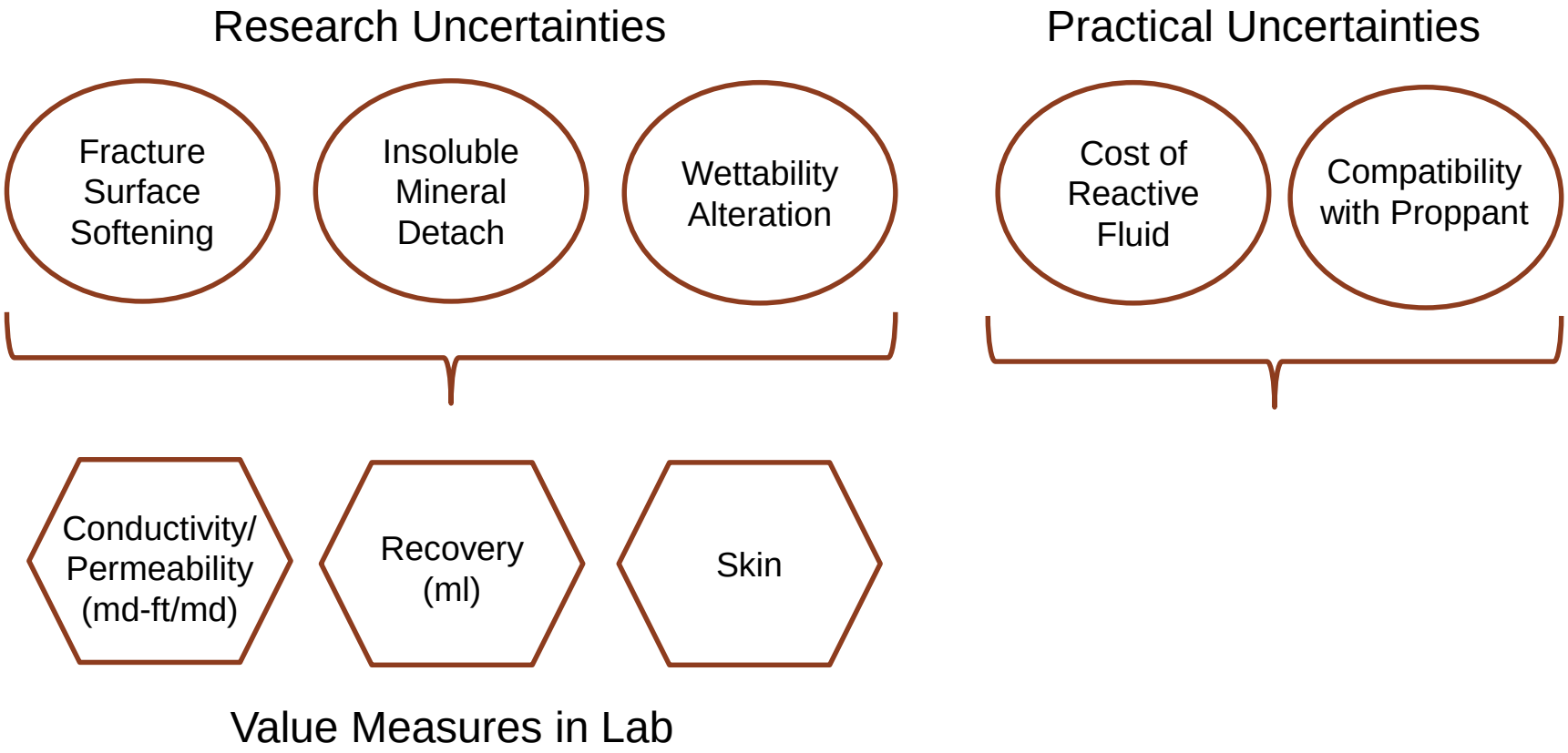
Research Uncertainties

- Fracture Surface Softening
- Insoluble Mineral Detach
- Wettability Alteration

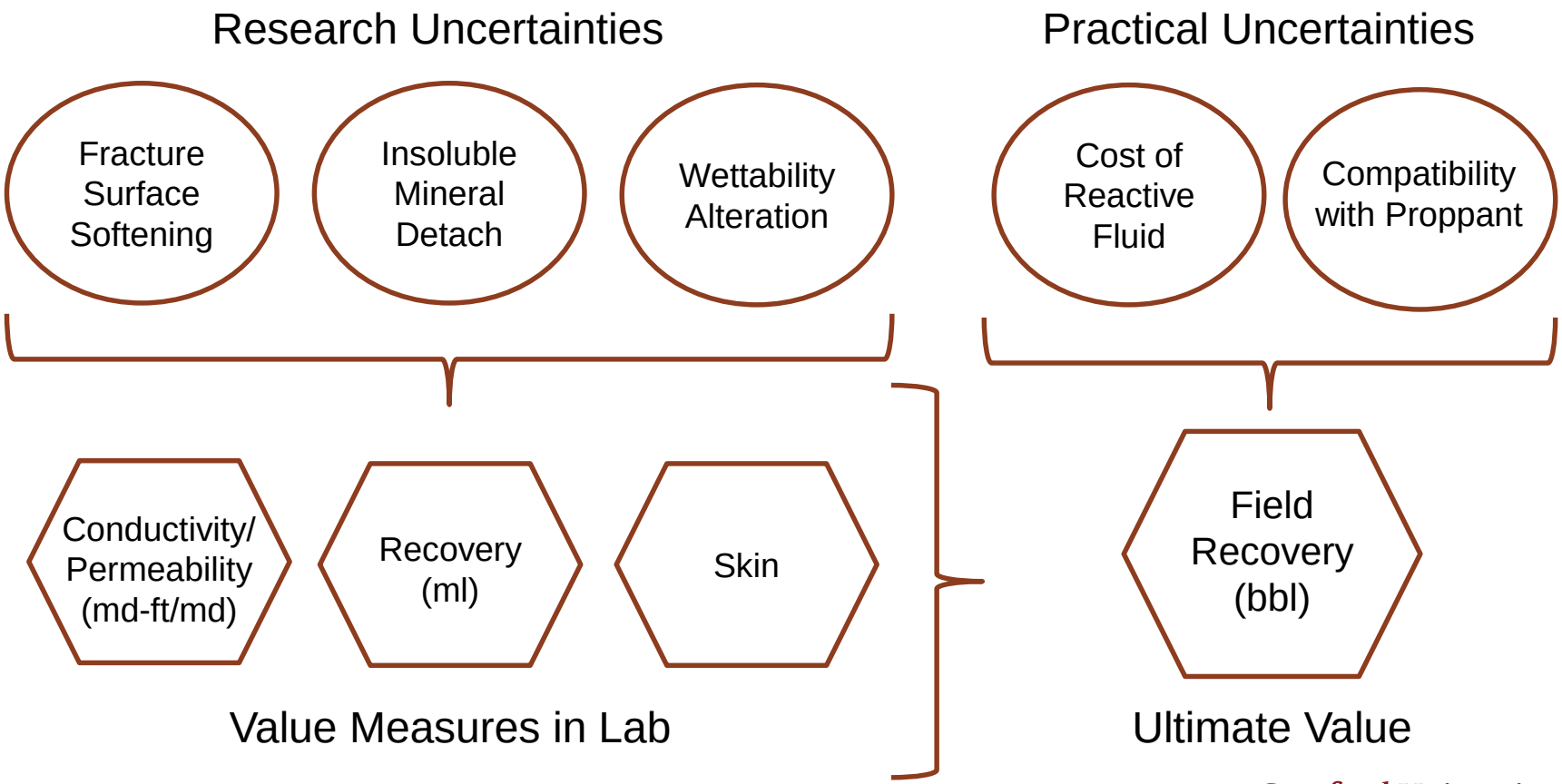
Practical Uncertainties

- Cost of Reactive Fluid
- Compatibility with Proppant

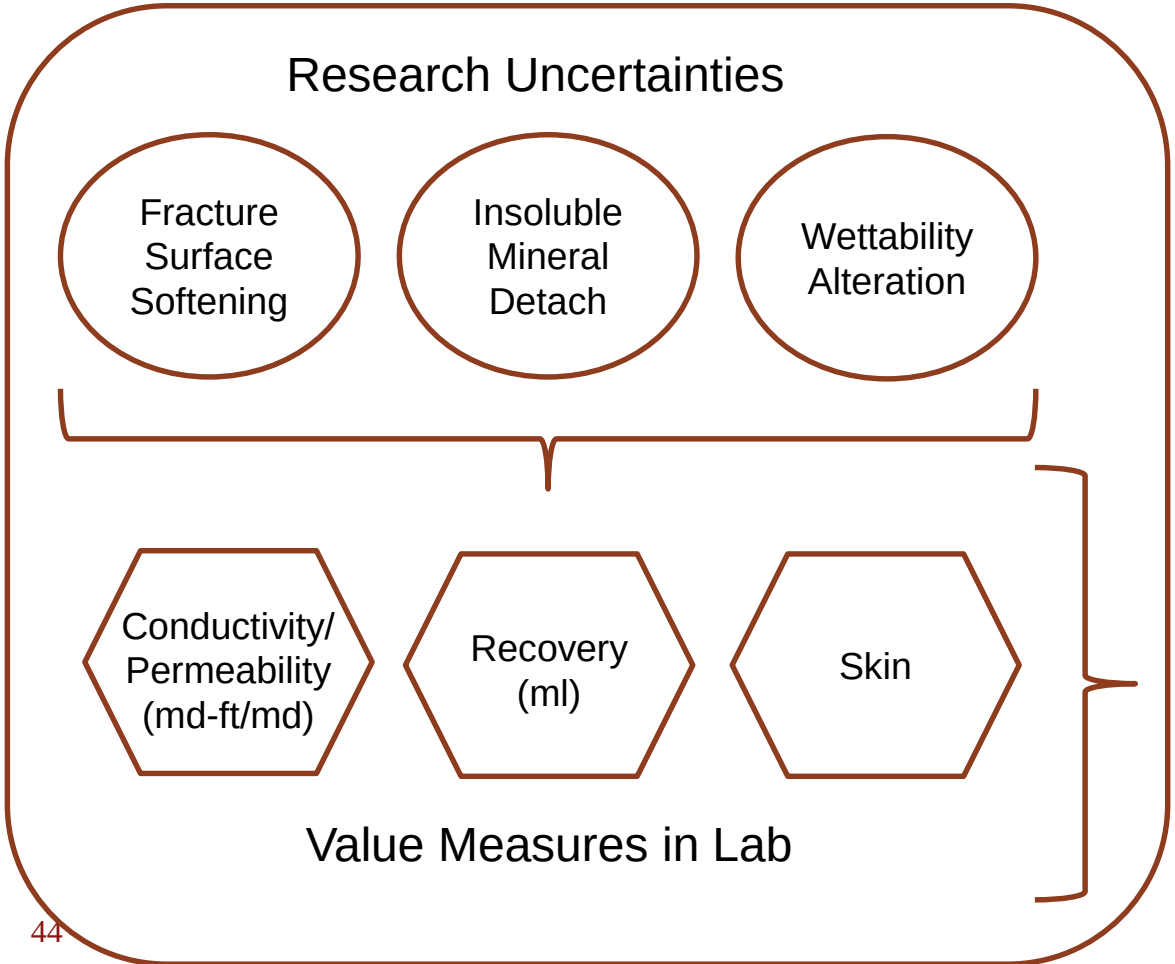
Framing… (3/3)


Research Uncertainties
Practical Uncertainties
Fracture Surface Softening
Insoluble Mineral Detach
Wettability Alteration
Cost of Reactive Fluid
Compatibility with Proppant
Conductivity/ Permeability (md-ft/md)
Recovery (ml)
Skin
Value Measures in Lab

Framing… (3/3)


Research Uncertainties
Practical Uncertainties
Fracture Surface Softening
Insoluble Mineral Detach
Wettability Alteration
Cost of Reactive Fluid
Compatibility with Proppant
Conductivity/ Permeability (md-ft/md)
Recovery (ml)
Skin
Field Recovery (bbl)
Value Measures in Lab
Ultimate Value

From an Experimentalist Standpoint…



What do we know?