

Relative Permeability in Reactive Carbonate Rock



Johnathan Moore

Research Scientist
Research and Innovation Center



Interpore 2021
May 31-June 4, 2021

Interpore 2021
Date Presented TBD

FRESH LOOK AT
D CEMENT

EOR Performance and
Mature Fi

De

Disclaimer

This project was funded by the Department of Energy, National Energy Technology Laboratory an agency of the United States Government, through a support contract. Neither the United States Government nor any agency thereof, nor any of its employees, nor the support contractor, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Authors and Contact Information



Johnathan Moore^{1,2}, Dustin Crandall¹, Paul Holcomb^{1,2}

¹National Energy Technology Laboratory, 3610 Collins Ferry Road, Morgantown, WV 26507, USA

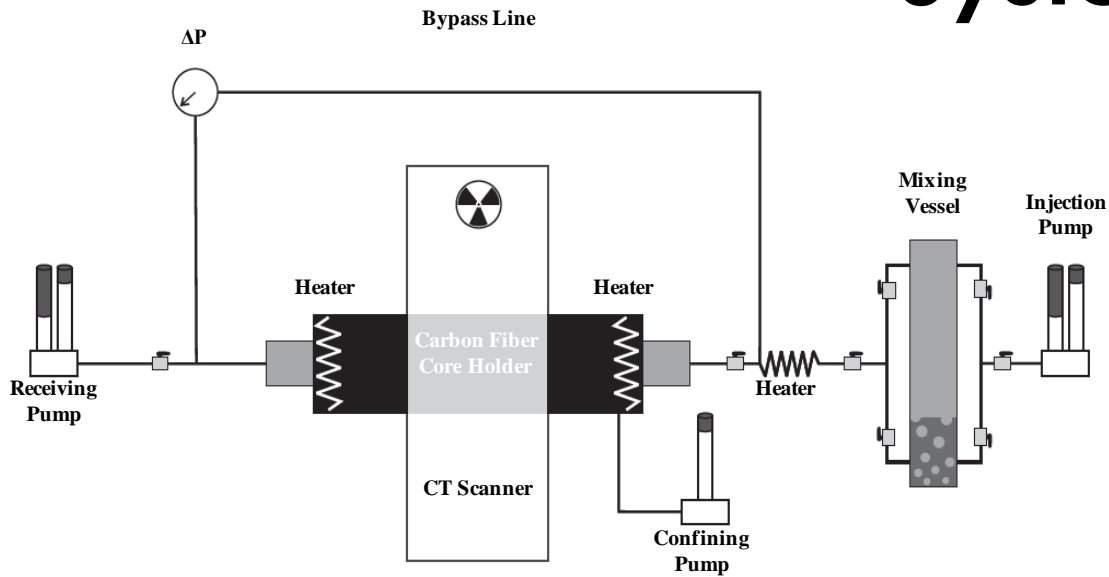
²NETL Support Contractor, 3610 Collins Ferry Road, Morgantown, WV 26507, USA

Emails:

Johnathan.Moore@netl.doe.gov, Dustin.Crandall@netl.doe.gov, Paul.Holcomb@netl.doe.gov

- **Relative Permeability (k_r):** the ratio of the effective permeability of a single fluid in a fluid mixture through a rock to the absolute permeability (k) of that fluid alone.
- **Unsteady State k_r :** Injection of one fluid into a rock core completely saturated with another fluid.
- **Characterization of fluid behavior and interaction in GCS reservoirs is essential to understanding long term safety and storage efficacy**
 - k_r is one of the fundamental parameters used to populate simulations to predict fluid migration and behavior
 - While k_r has been largely characterized and parameterized in traditional 'unreactive' geologic reservoirs, carbonates are largely uncharacterized due to their reactive nature
 - Carbonates are highly reactive with even weak acids, such as carbonic acid, which readily dissolves the mineral constituents and increases permeability & porosity
 - Carbonate reservoirs are readily available and often have appreciable permeability/porosity (re petroleum in the Arabian Peninsula and drinking water aquifers)

System Design



Schematic of experimental system flow through system inside of medical computed tomography scanner.

Experimental Conditions

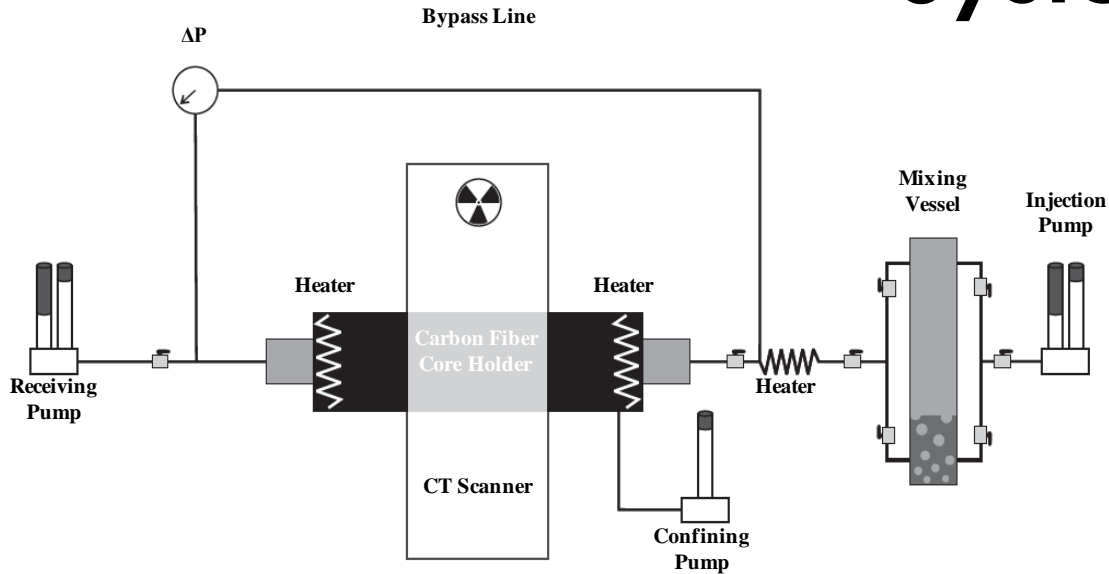
Temperature: 63.3 °C

Brine Composition (By weight %): 5% KI, 3% KCl

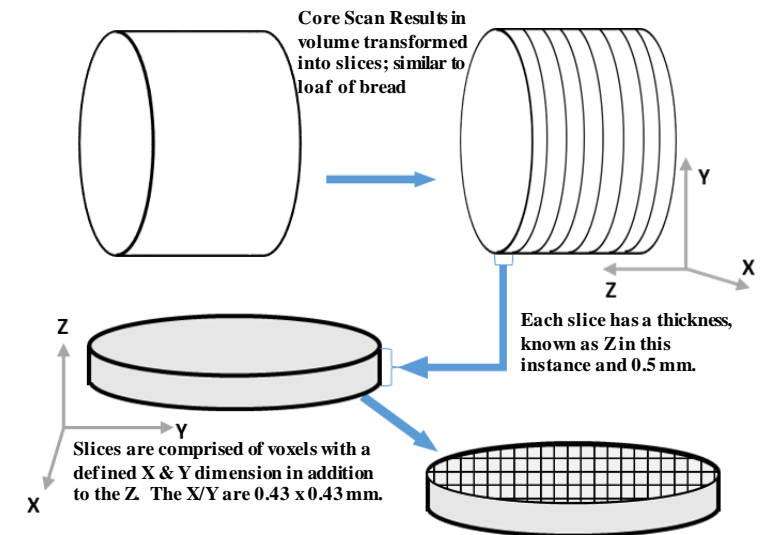
Pore Pressure: 9.65 Mpa

Overburden Pressure: 13.79 MPa

System Design



Schematic of experimental system flow through system inside of medical computed tomography scanner.



Schematic of CT scan within CT system illustrating data configuration.

Experimental Conditions

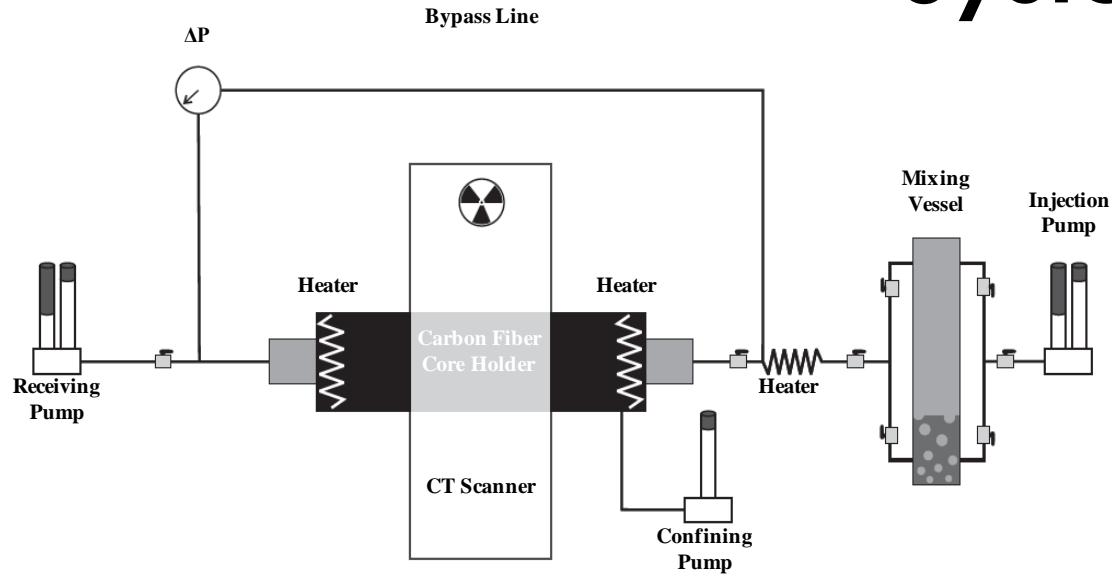
Temperature: 63.3 °C

Brine Composition (By weight %): 5% KI, 3% KCl

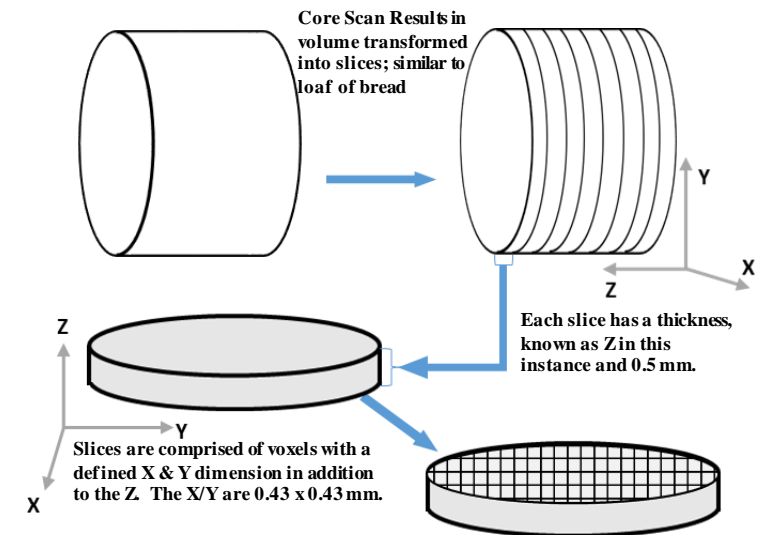
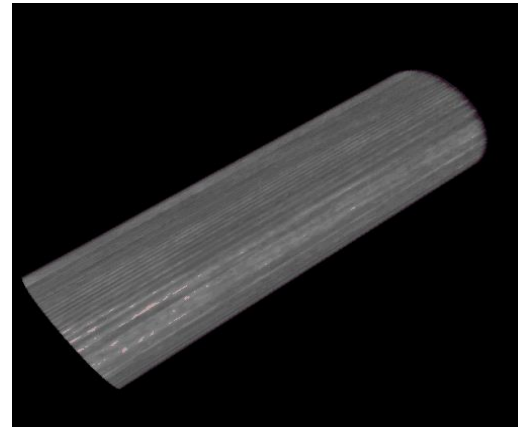
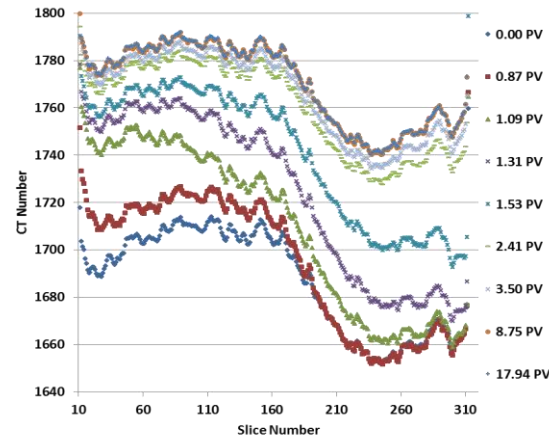
Pore Pressure: 9.65 Mpa

Overburden Pressure: 13.79 MPa

System Design



Schematic of experimental system flow through system inside of medical computed tomography scanner.



Schematic of CT scan within CT system illustrating data configuration.

Experimental Conditions

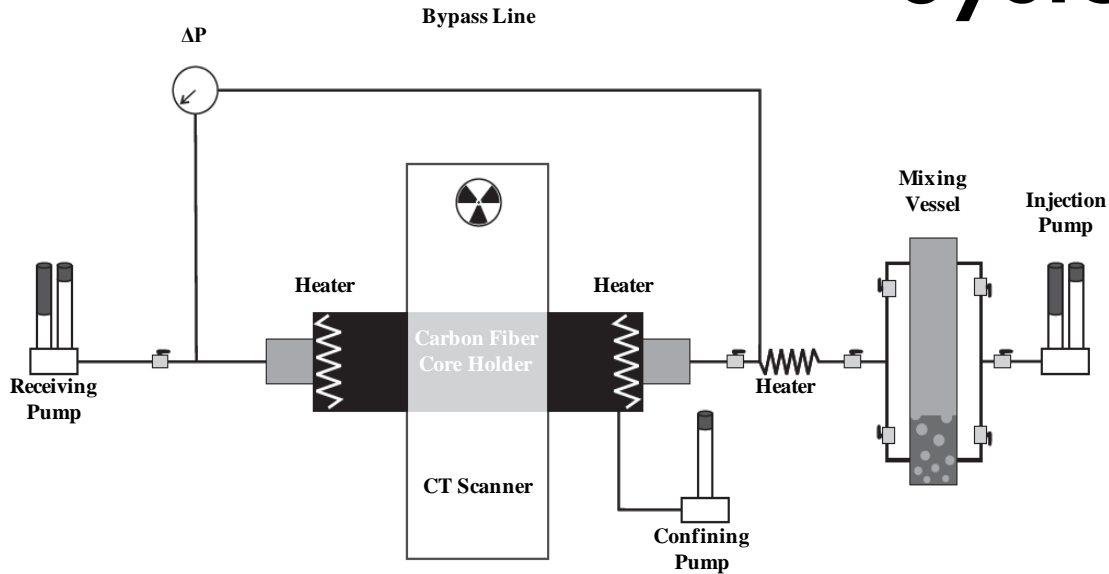
Temperature: 63.3 °C

Brine Composition (By weight %): 5% KI, 3% KCl

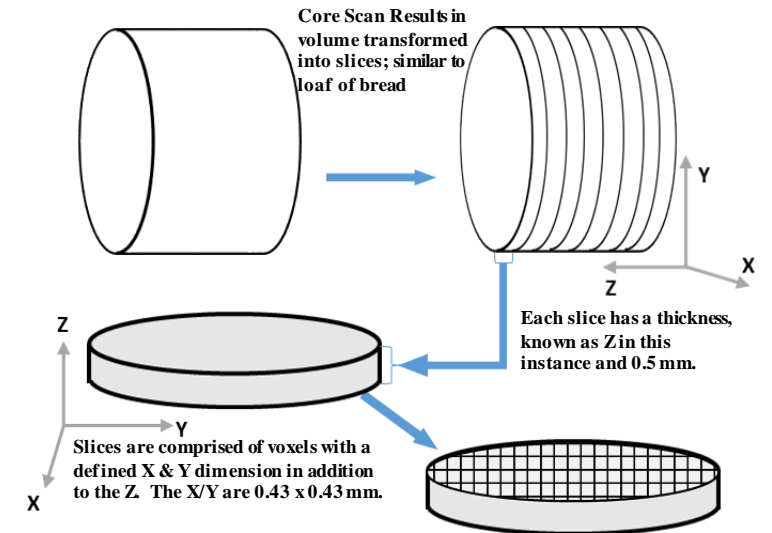
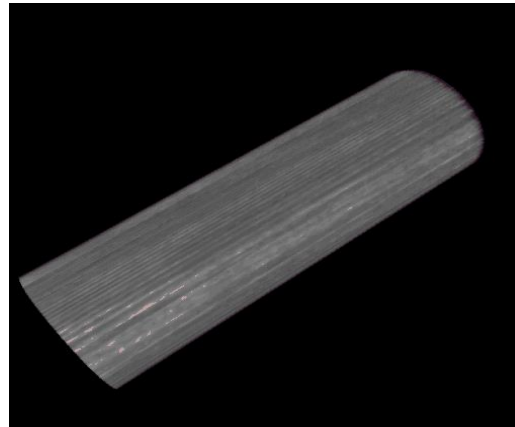
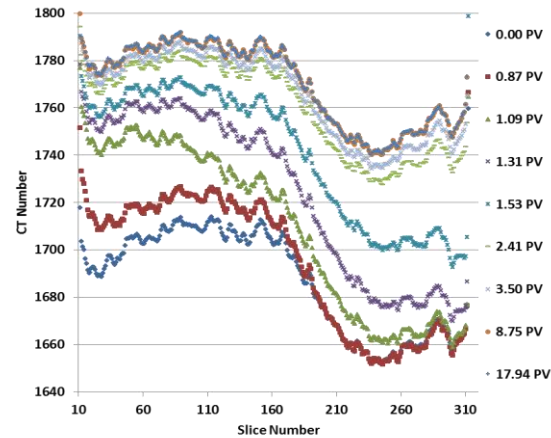
Pore Pressure: 9.65 MPa

Overburden Pressure: 13.79 MPa

System Design



Schematic of experimental system flow through system inside of medical computed tomography scanner.



Schematic of CT scan within CT system illustrating data configuration.

Experimental Conditions

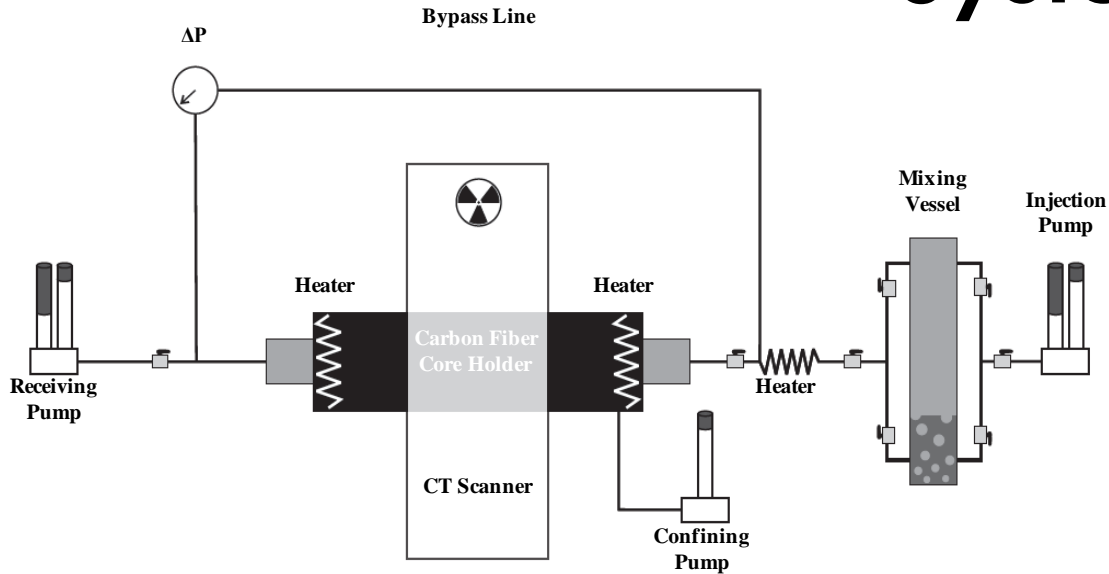
Temperature: 63.3 °C

Brine Composition (By weight %): 5% KI, 3% KCl

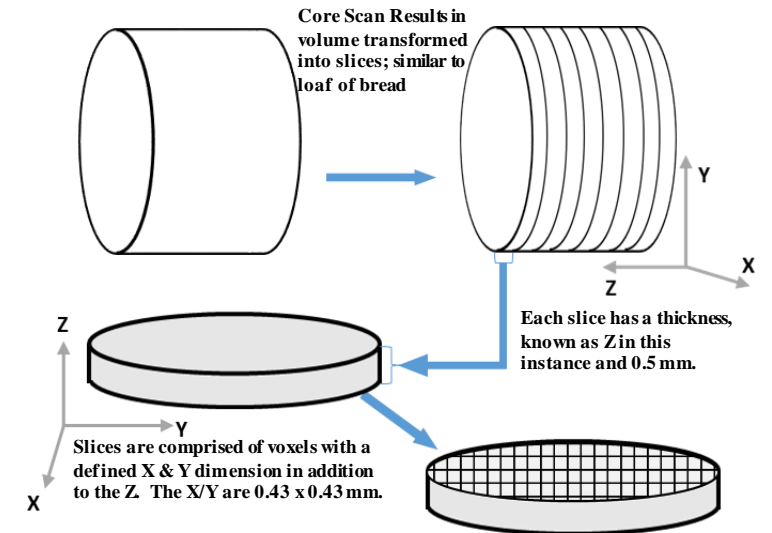
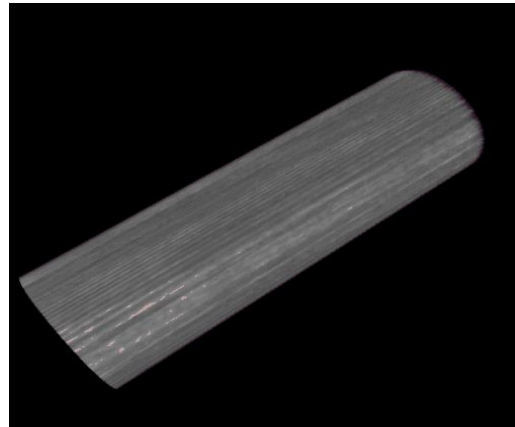
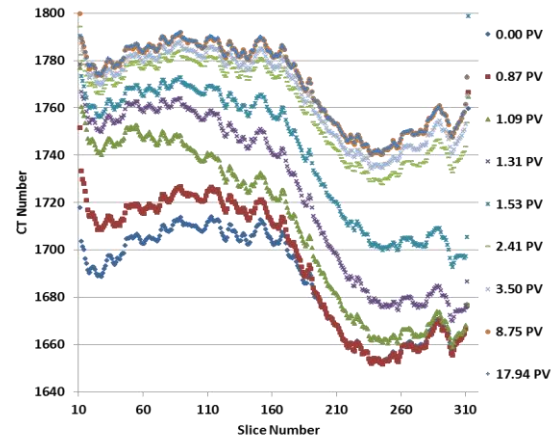
Pore Pressure: 9.65 MPa

Overburden Pressure: 13.79 MPa

System Design



Schematic of experimental system flow through system inside of medical computed tomography scanner.



Schematic of CT scan within CT system illustrating data configuration.

Experimental Conditions

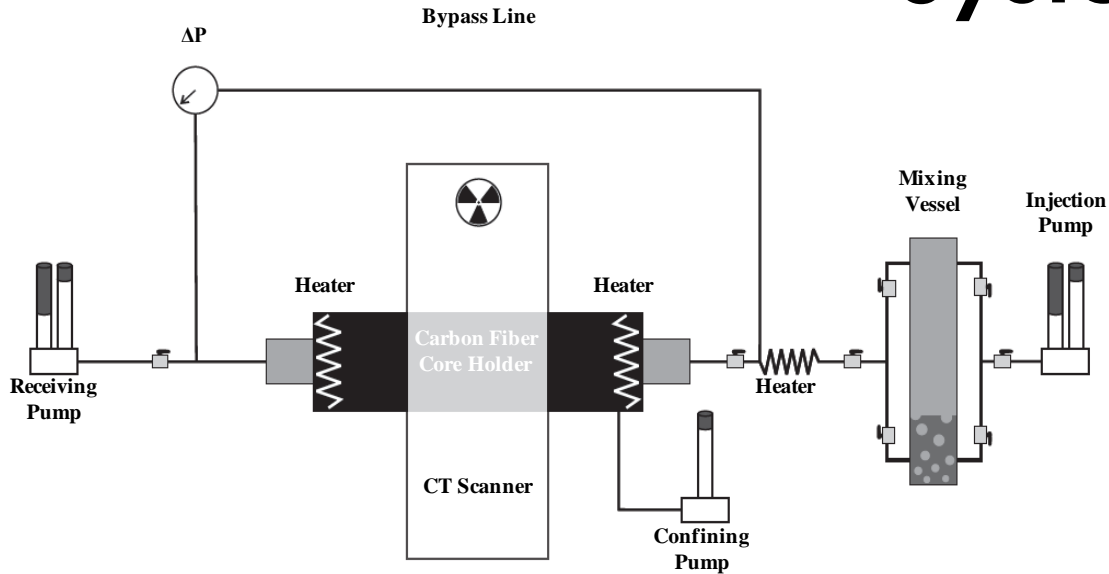
Temperature: 63.3 °C

Brine Composition (By weight %): 5% KI, 3% KCl

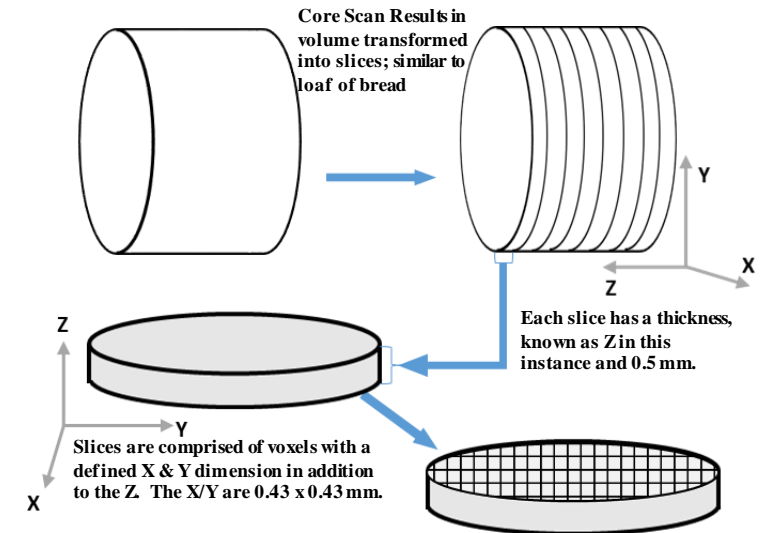
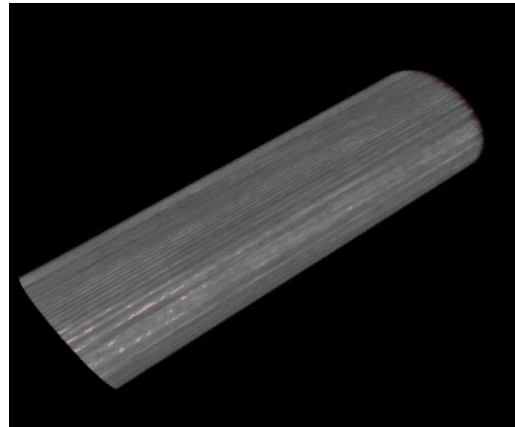
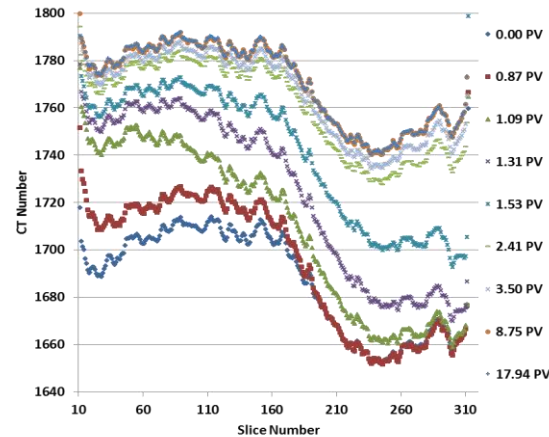
Pore Pressure: 9.65 MPa

Overburden Pressure: 13.79 MPa

System Design



Schematic of experimental system flow through system inside of medical computed tomography scanner.



Schematic of CT scan within CT system illustrating data configuration.

Experimental Conditions

Temperature: 63.3 °C

Brine Composition (By weight %): 5% KI, 3% KCl

Pore Pressure: 9.65 MPa

Overburden Pressure: 13.79 MPa

System Design

Bypass Line

ΔP

General Experimental Standards & Limits

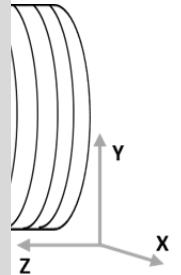
- Toshiba Aquilion System
 1. Produces DICOM image format in 16-bit grayscale
 2. Calibrated to known standards relative to HU
 3. 8-slice fan beam helical scanner
 4. Scans < 10 seconds at 10-20 second intervals
 5. Resolution at 0.43x0.43x0.5 mm
- Flow System
 1. Carbon Fiber Hassler style core holder
 2. Buna-N sleeves for confining membrane
 3. Teledyne ISCO 500 HP pumps for pressure/injection
 4. Rosemount DP gauges (3051CD)
 5. Clamshell heaters to apply heat to both coil and core holder

Slice Number

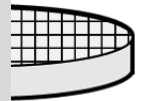
CT Number

Schematic of exper

Receiving
Pump



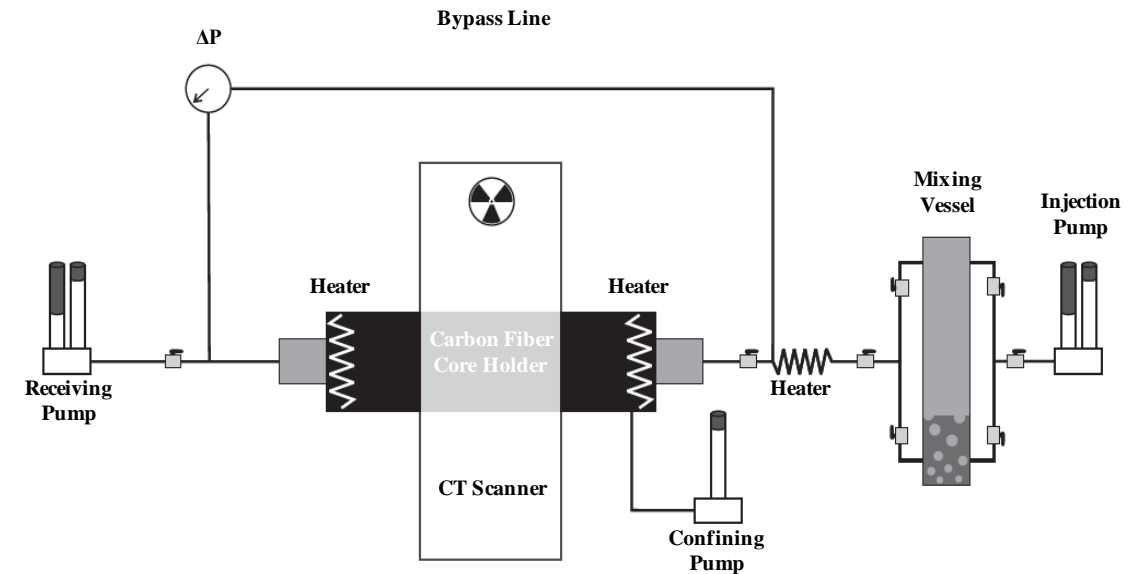
e has a thickness,
Z in this
and 0.5 mm.



data configuration.

1, 3% KCl

NETL Study Considerations



Schematic of experimental system flow through system inside of medical computed tomography scanner.

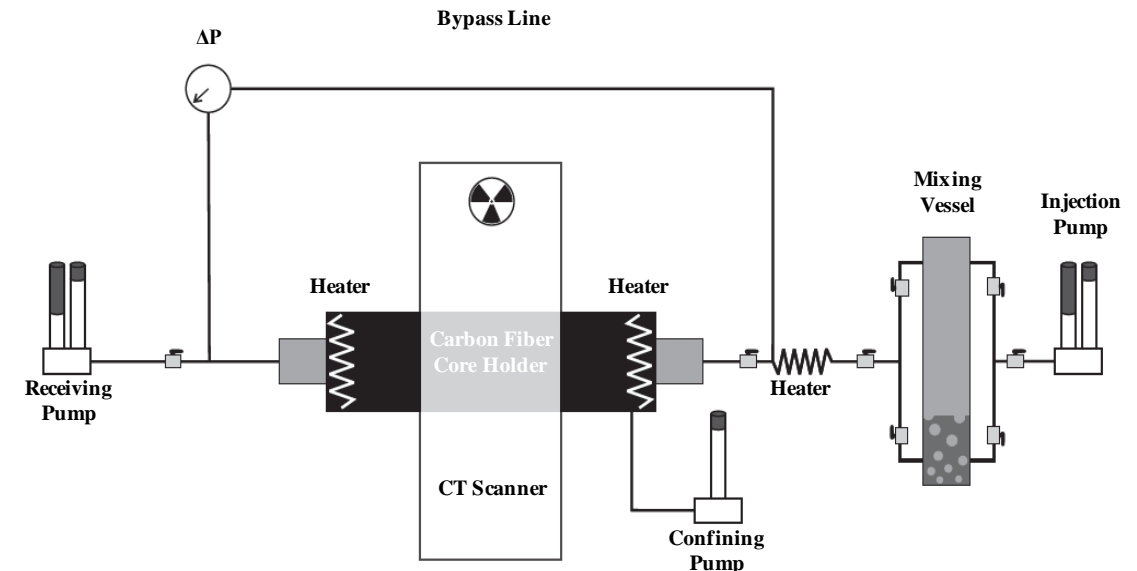
NETL Study Considerations

Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

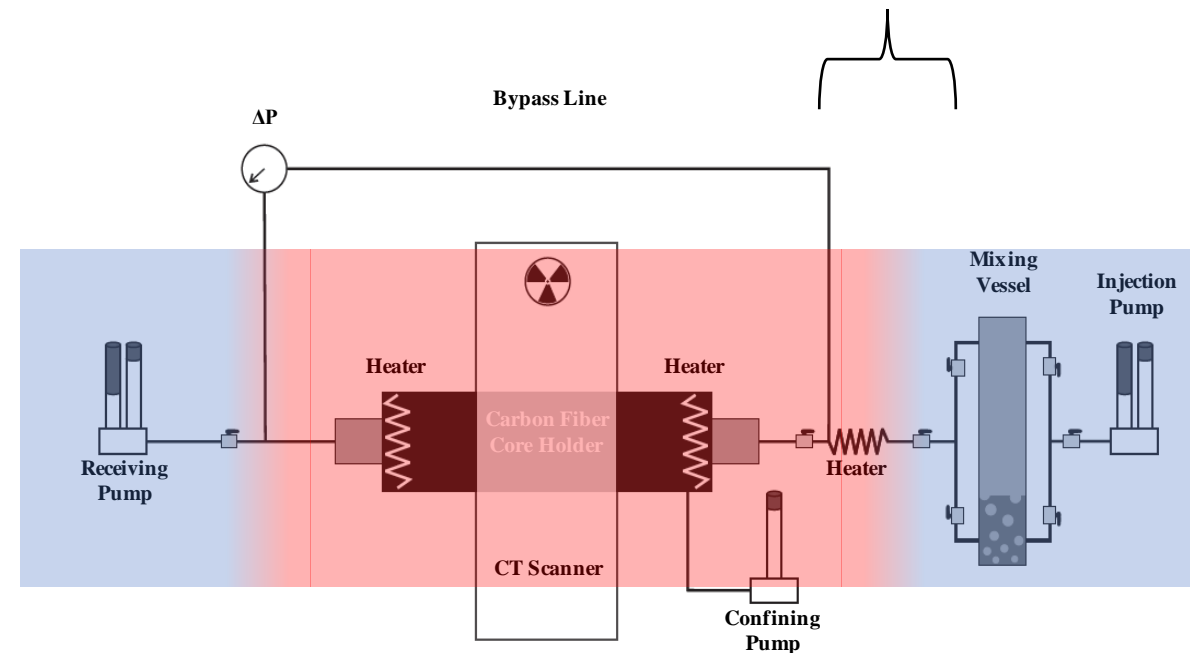
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.


NETL Study Considerations

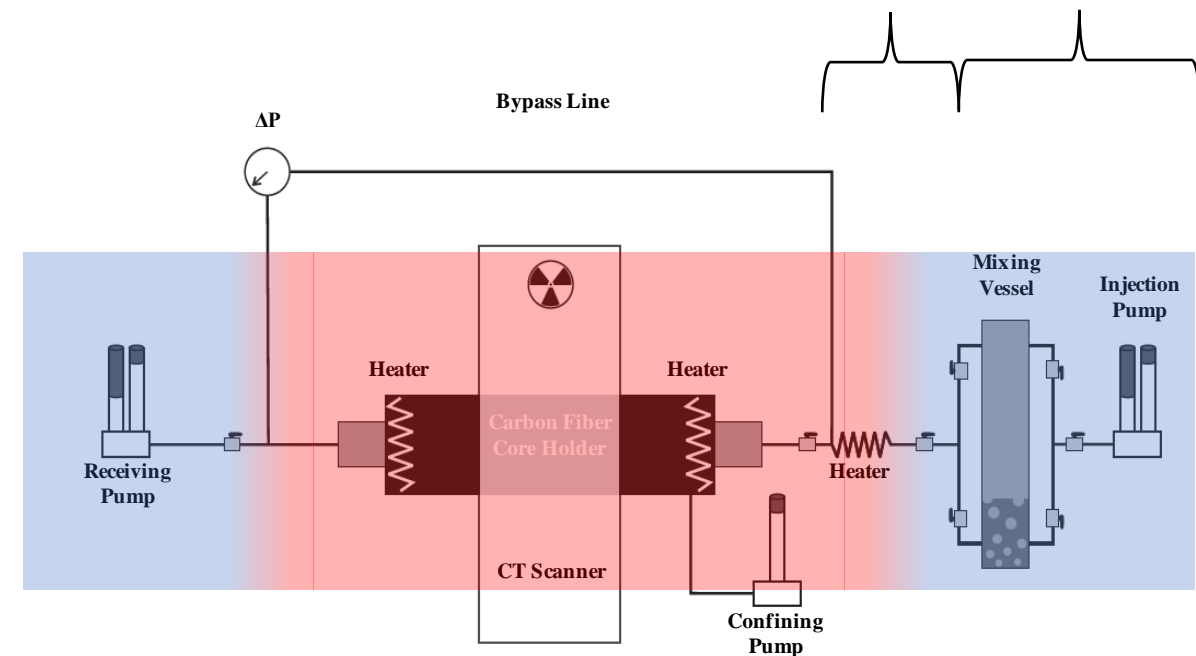
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

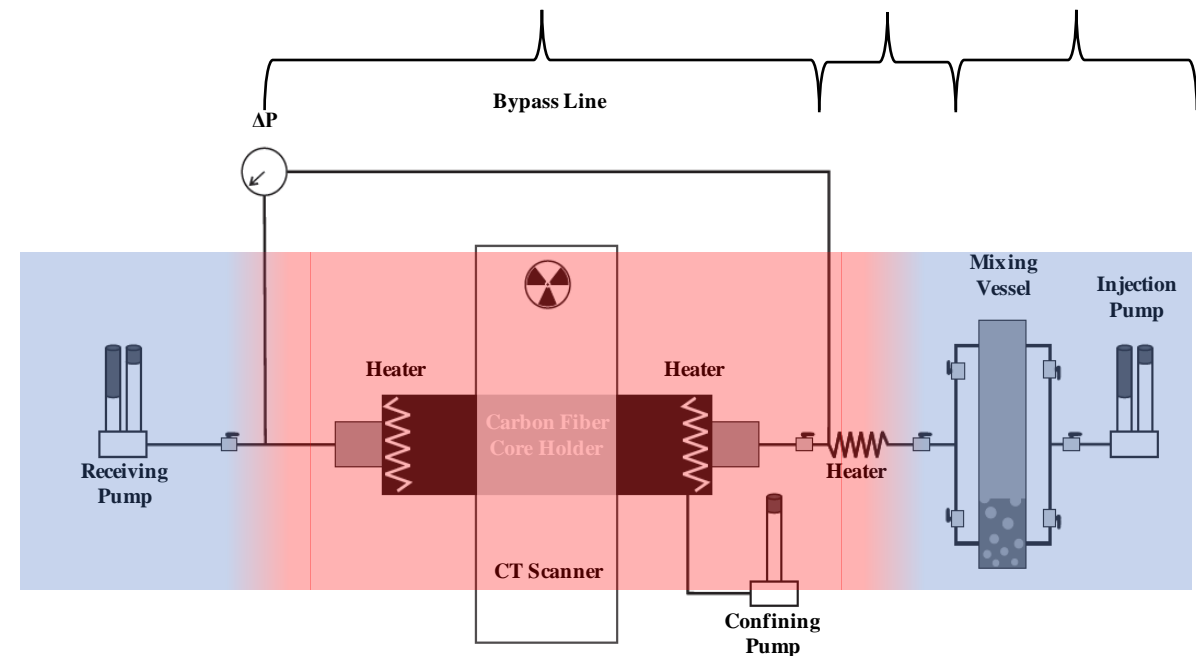
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

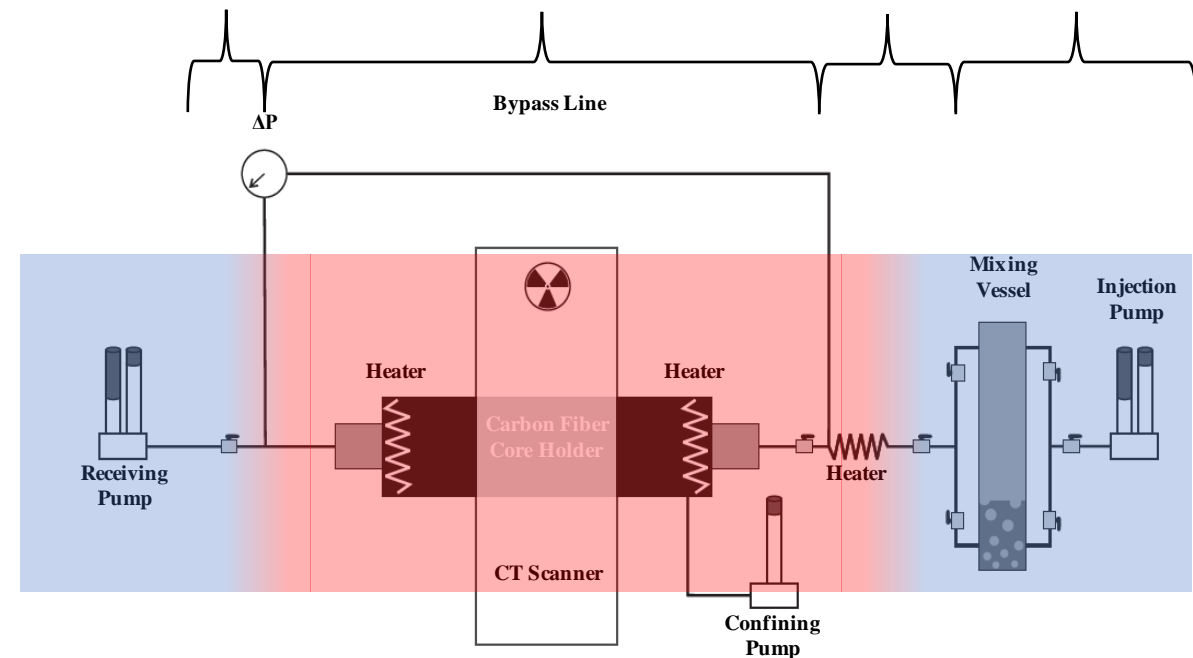
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

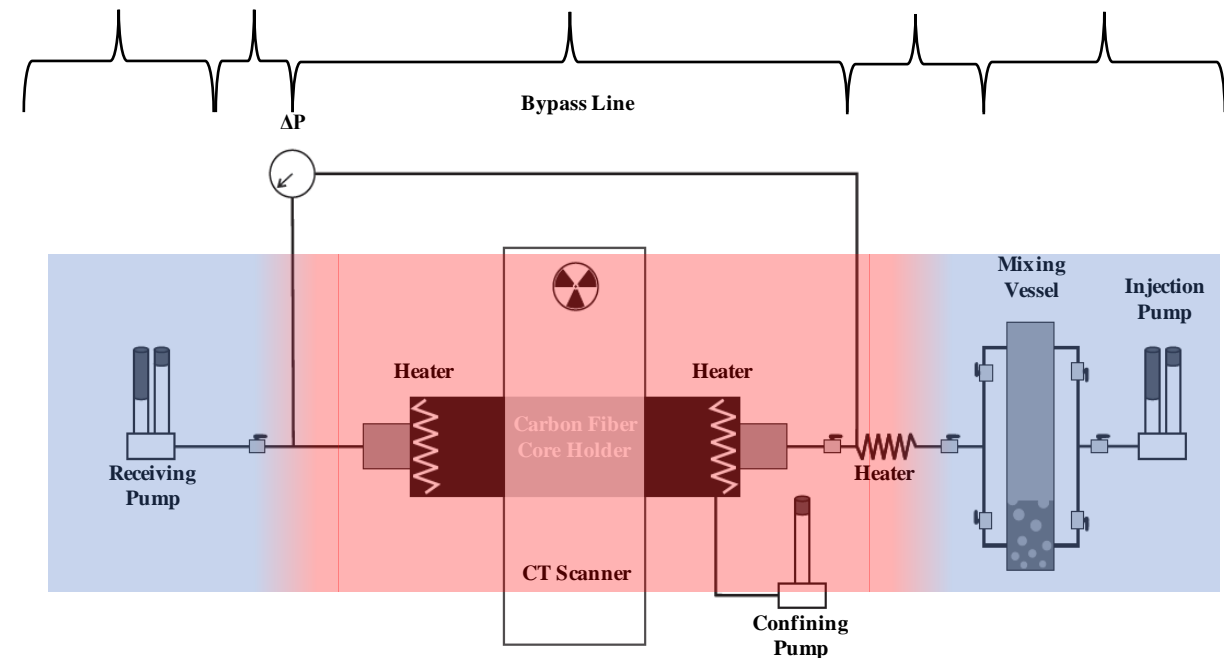
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

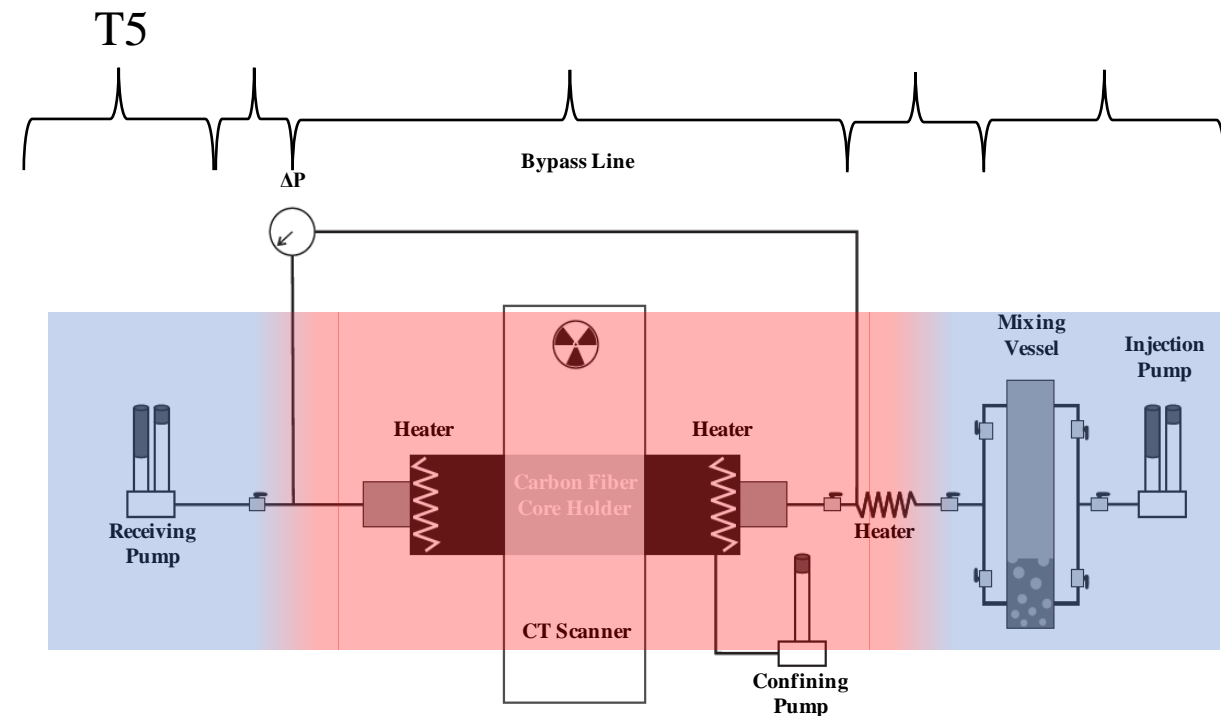
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.


NETL Study Considerations

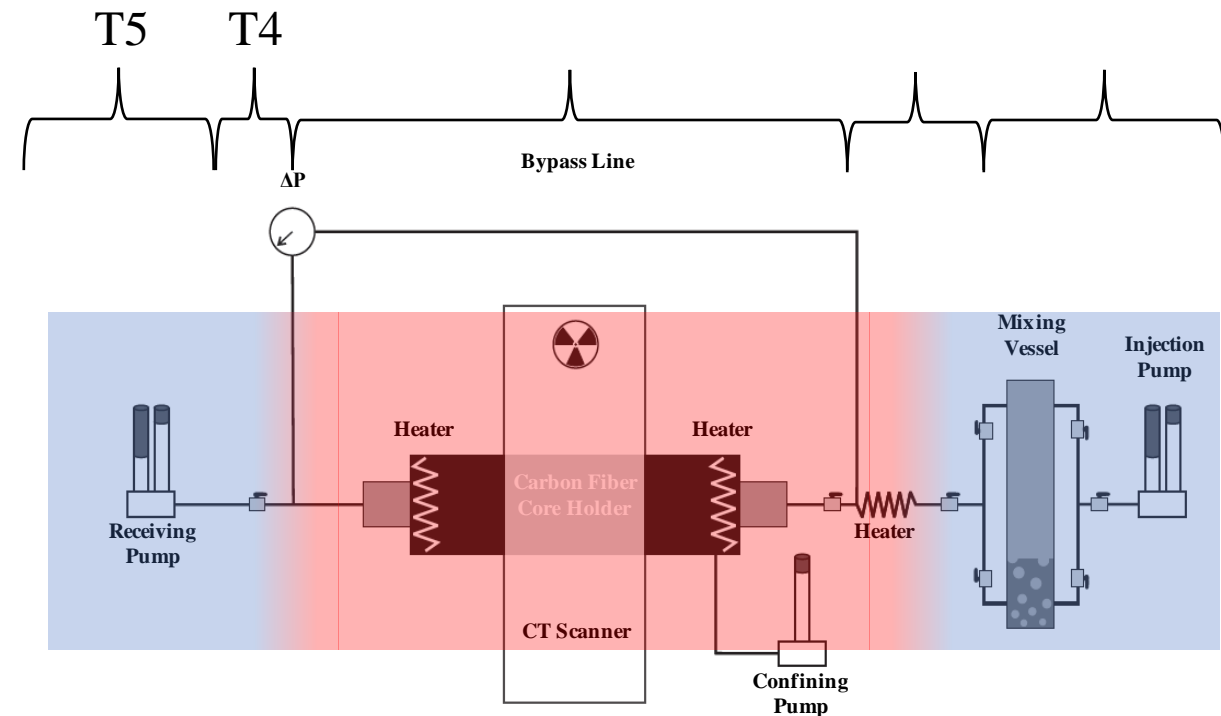
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

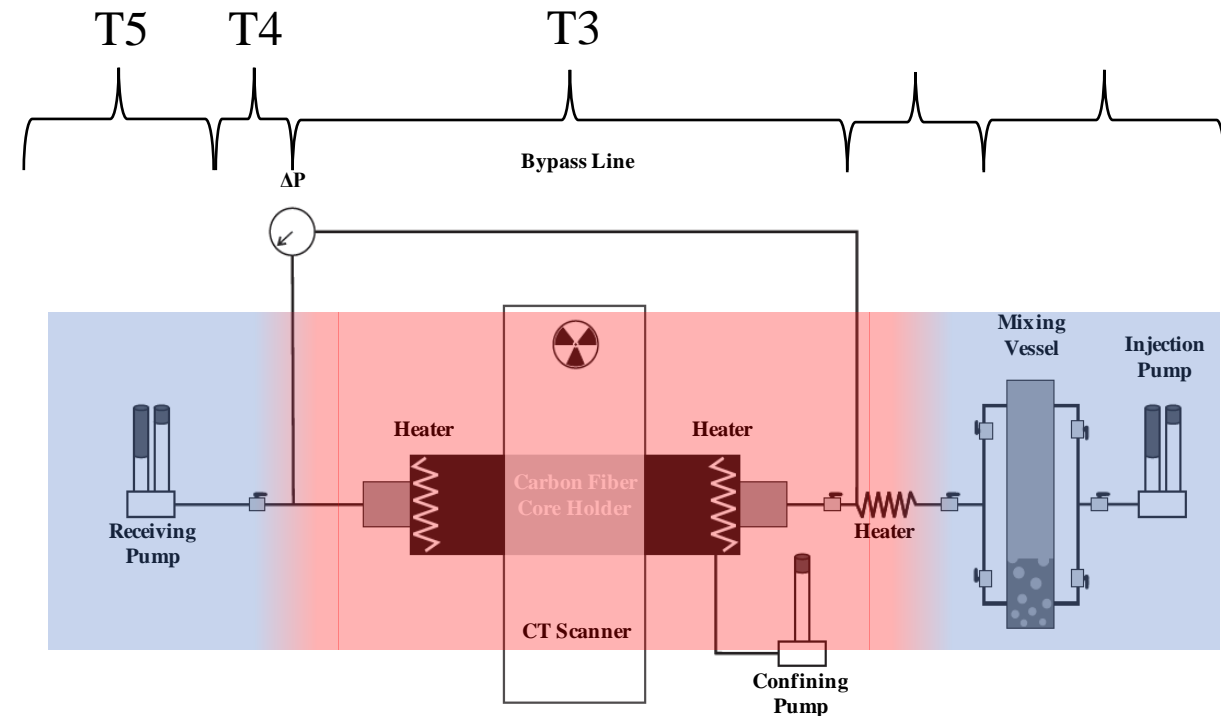
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

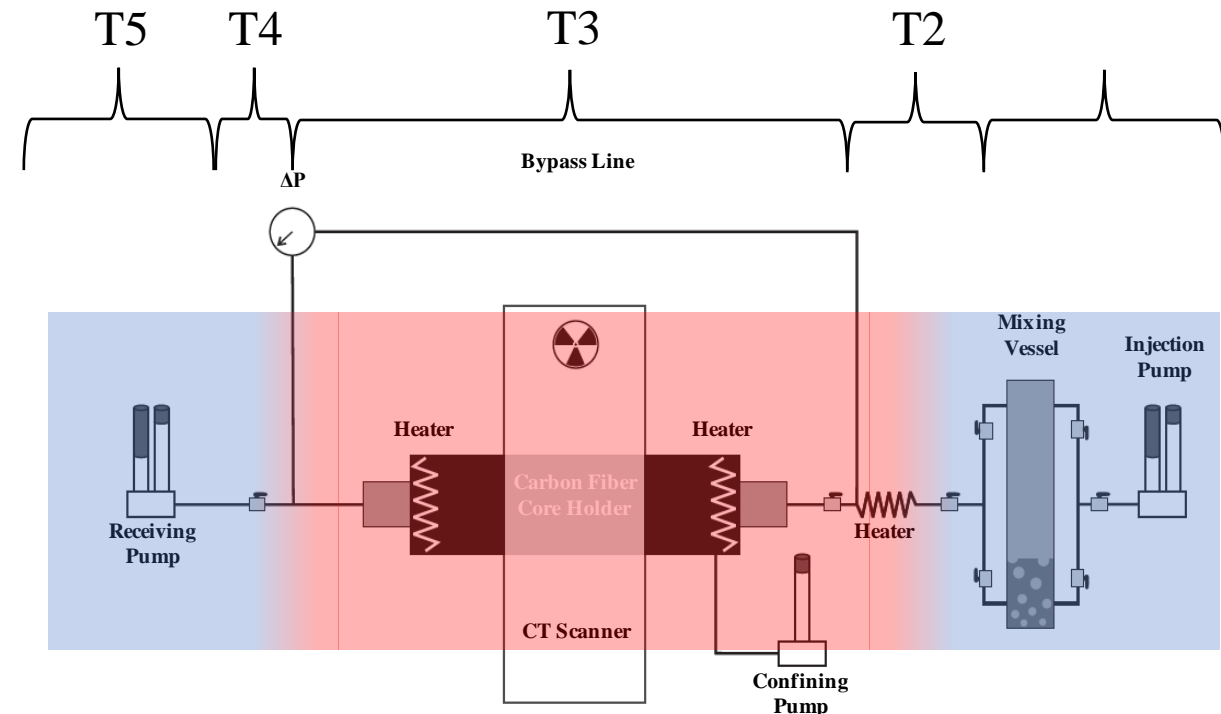
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

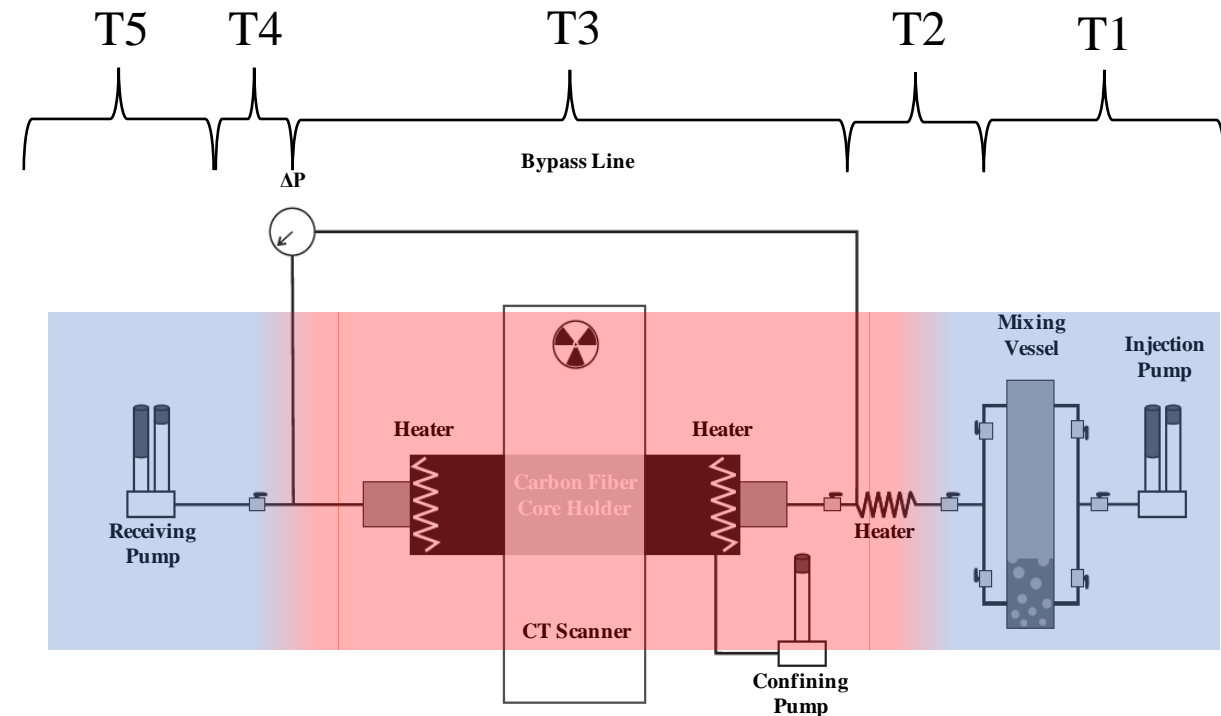
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

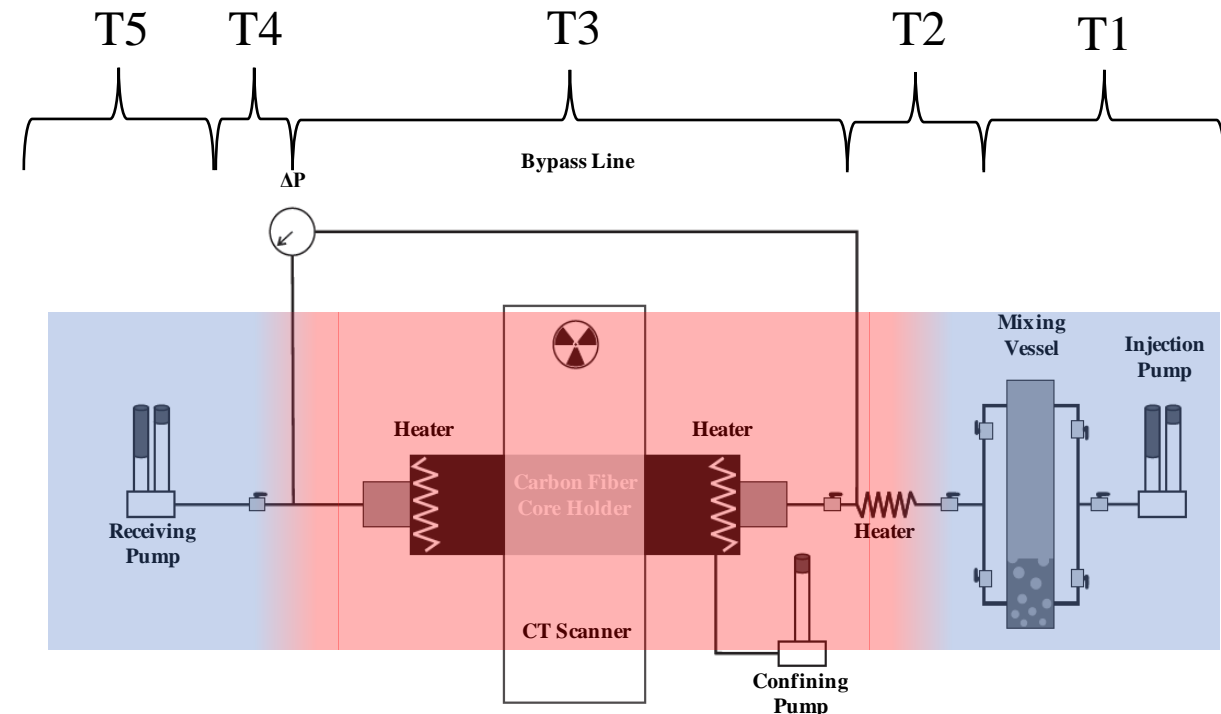
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.


NETL Study Considerations

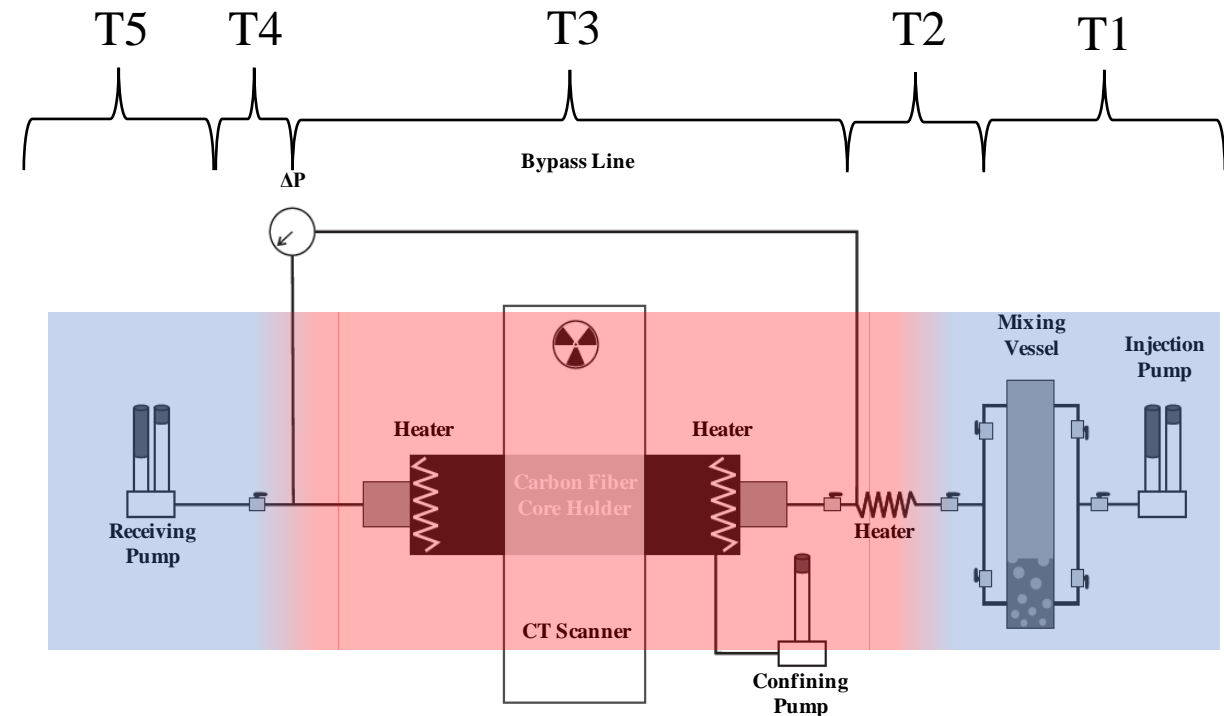
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

NETL Study Considerations

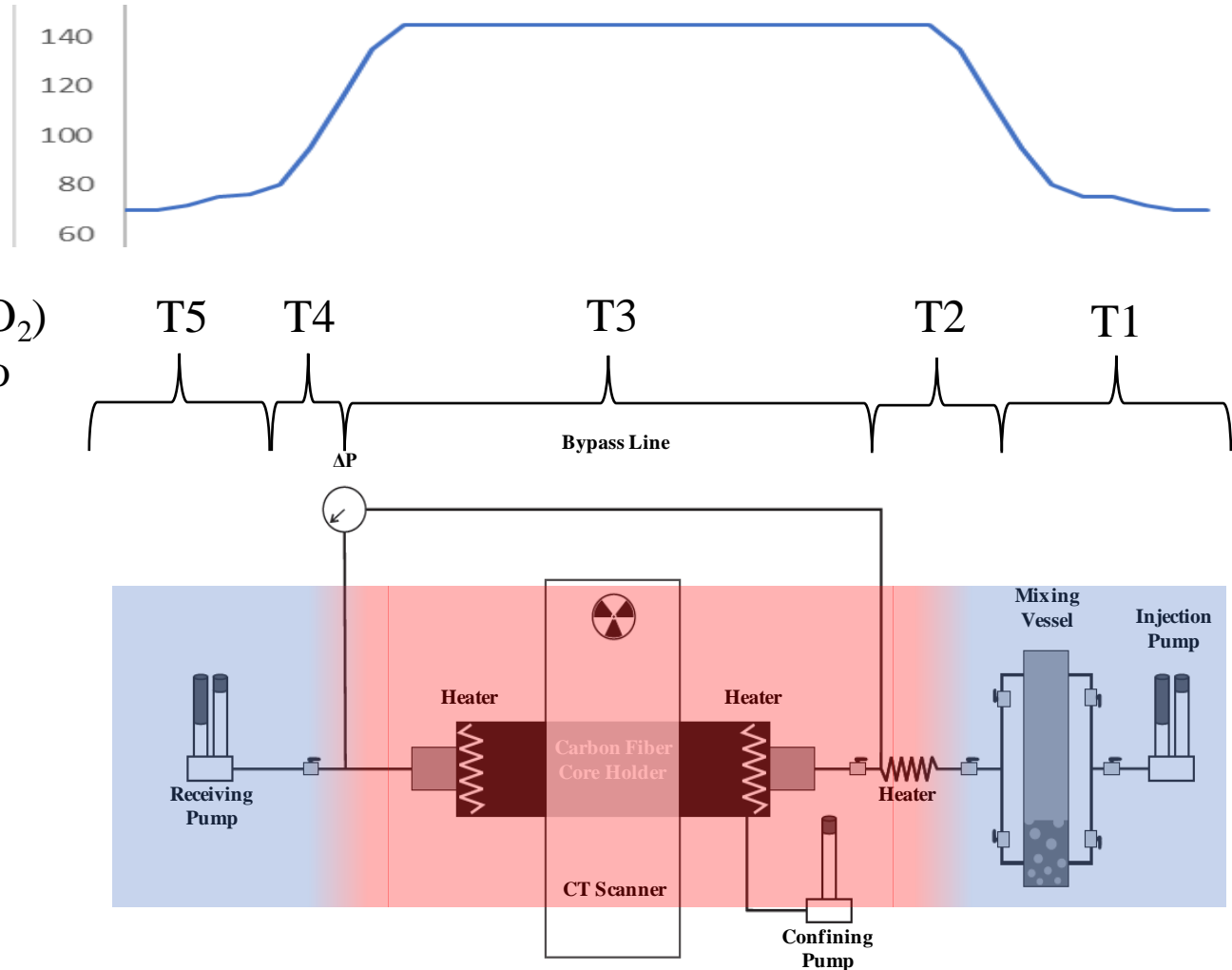
Assumptions of Toth et al.:

- Two Phase System
 1. E.g. the phase doesn't change
- Fluids are immiscible
- Temperature is constant

Our System:

- We are creating a phase change $\text{CO}_2(\text{l})$ to $\text{CO}_2(\text{scCO}_2)$ just before the core holder and then reverting back to $\text{CO}_2(\text{l})$ in the receiving pumps
- Fluids are not immiscible
 1. They are equilibrated*
- Temperature is not constant
 1. Starts at ambient (T1)
 2. Heats to ~145F (T2)
 3. Stays heated for flow through (T3)
 4. Cools to ambient (T4)
 5. Ends at ambient (T5)

 Liquid
 Supercritical



Schematic of experimental system flow through system inside of medical computed tomography scanner.

Phase Change Implications for Flow Rate

- When going from liquid to supercritical, the CO₂ effective Z increases (Peng & Robinson, 1976).

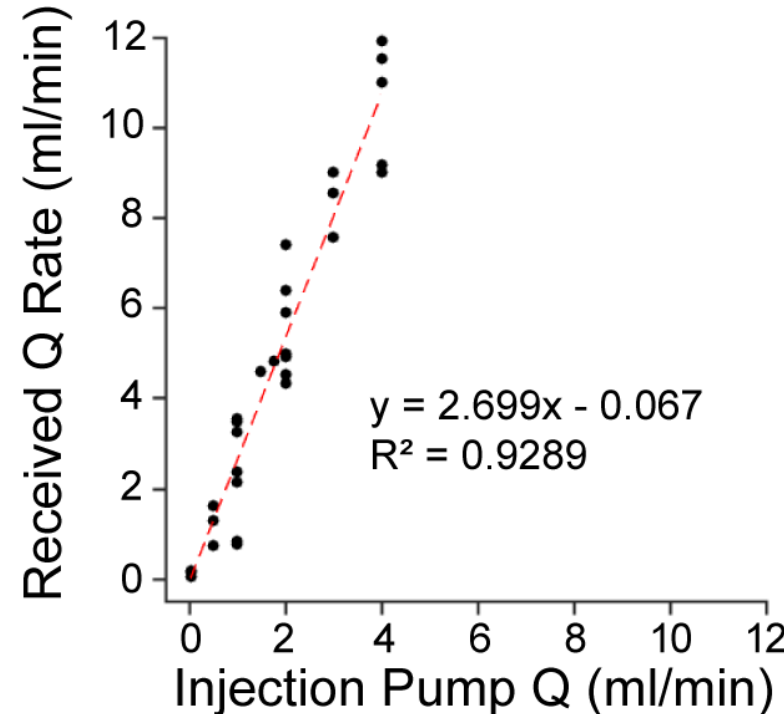
T=70F.....Z=0.214
T=145.9F.....Z=0.585

➔ The backpressure pump maintains a constant pressure = the fluid can expand via:

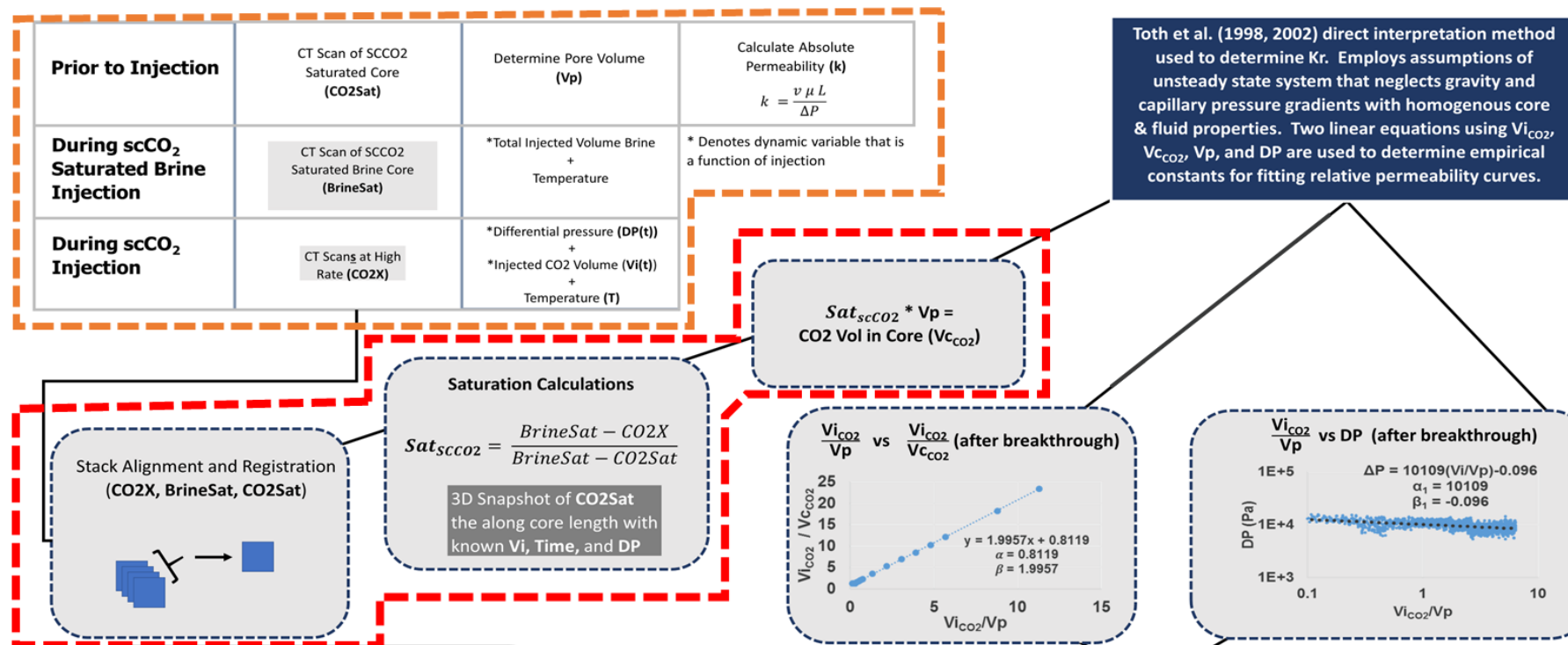
$$Z = \frac{V}{V-b} - \frac{a}{VRT-2RTb-\left(\frac{RTb^2}{V}\right)}$$

➔ **The volumetric expansion results in a higher flow rate within the core than what is being initiated with the pump**

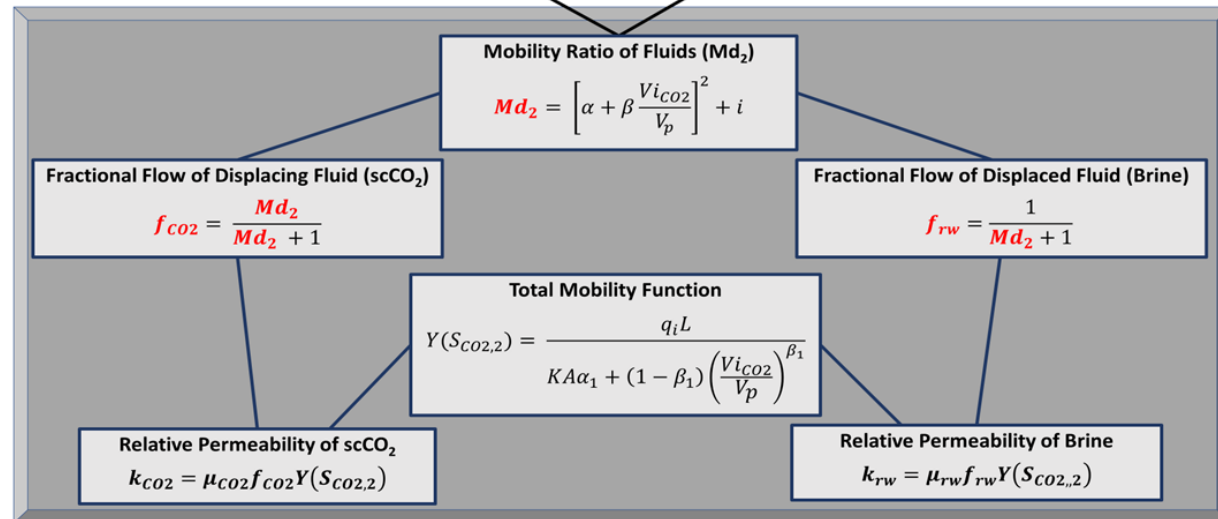
- Since injection rate is constant, conversion of CO₂(l) to scCO₂ should be constant
- The 26 flow tests available were evaluated based on backpressure pump receiving rate
 - Data was evaluated from core contact to breakthrough
 - During this timeframe the only fluids that are present in the core are Brine and scCO₂
 - Incompressible brine is displaced by scCO₂ which in turn gives us the rate of scCO₂ injection rate



- Clear agreement regardless of lithology, absolute permeability, or flow rate
- Illustrates a consistent state conversion within the system that results in a higher flow rate through the core



Terminology	
scCO ₂	supercritical CO ₂
Sat _{scCO₂}	saturation of supercritical CO ₂
k	permeability (cm ²)
A	core cross-sectional area (cm ²)
L	core length (cm)
T	temperature (°C)
DP	differential pressure across rock core (Pa)
q _i	flow rate (cm ³ /min)
α	empirical constant, dimensionless
β	empirical constant, dimensionless
α ₁	empirical constant (Pa)
β ₁	empirical constant, dimensionless
f _{CO₂}	fractional fluid flow of scCO ₂ , dimensionless
f _{rw}	fractional fluid flow of brine, dimensionless
V _p	pore volume (ml)
V _{iCO₂}	scCO ₂ volume injected (ml)
V _{cCO₂}	volume of scCO ₂ in the rock core (ml)
CO ₂ Sat	Computed tomography scan of scCO ₂ saturated core
BrineSat	Computed tomography scan of brine saturated core
CO ₂ X	Computed tomography scans of scCO ₂ injection into brine saturated core
M _{d2}	mobility ratio of fluids, dimensionless
k _{scCO₂}	scCO ₂ relative permeability
k _{rw}	brine relative permeability
μ _{CO₂}	viscosity of scCO ₂ , (Pa*s)
μ _{rw}	viscosity of brine, (Pa*s)

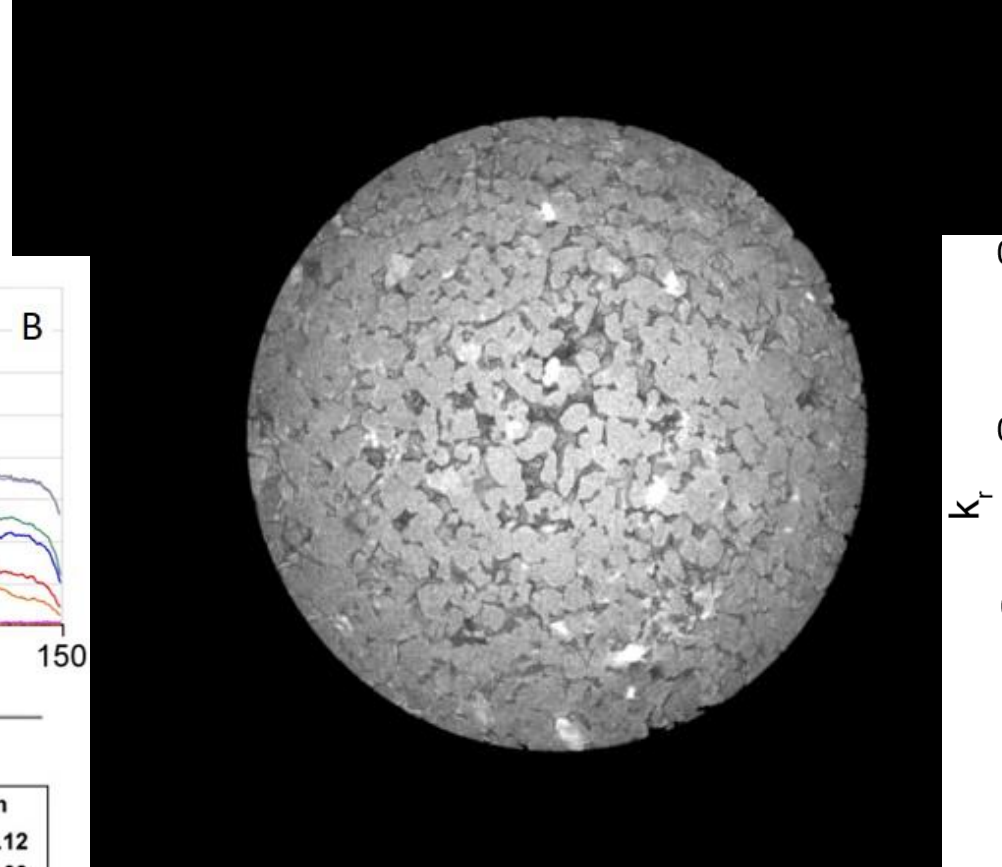
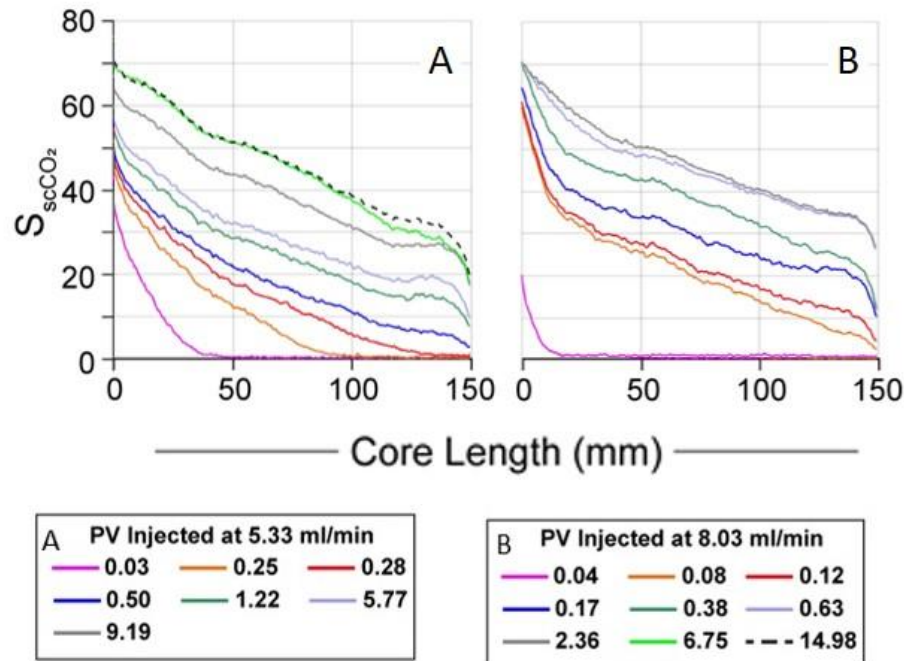


Non-Reactive kr

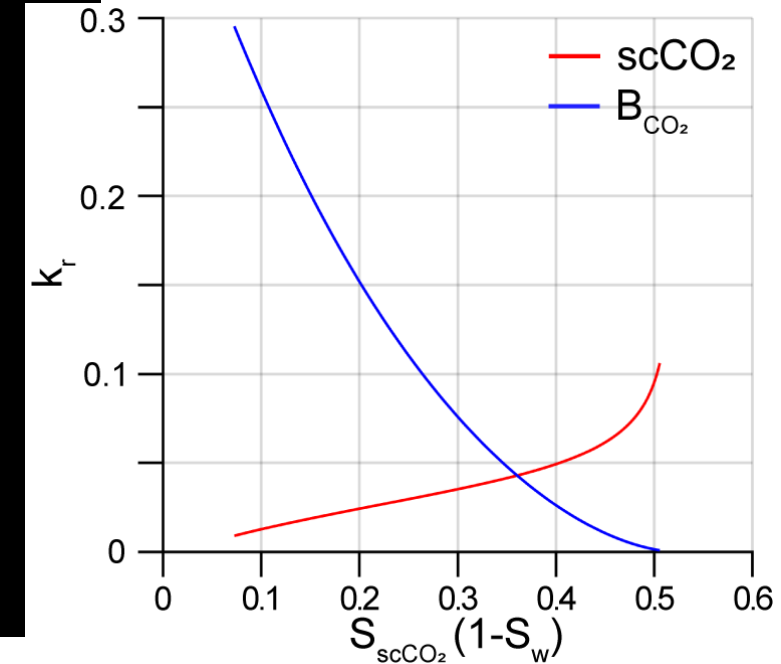
Berea Sandstone

- PV 57.1 ml
- k 424 mD
- \emptyset 18.8%

Saturation vs PV Injected

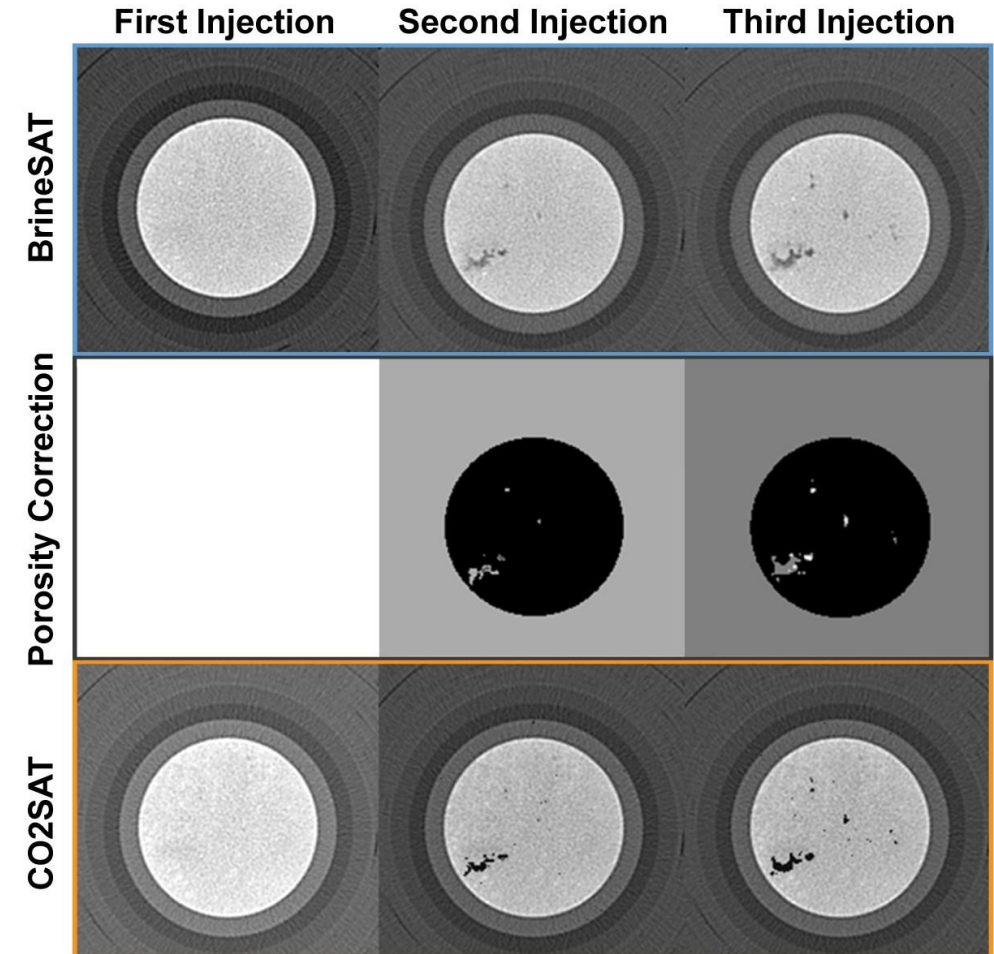


Example k_r curve

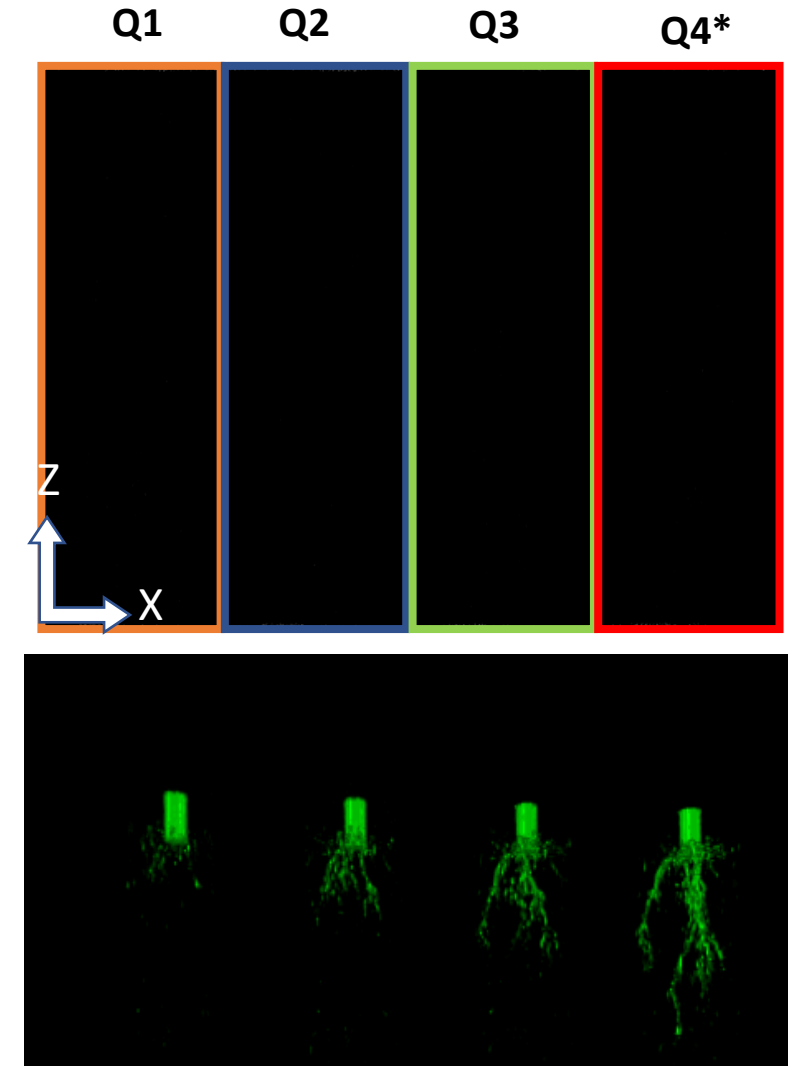
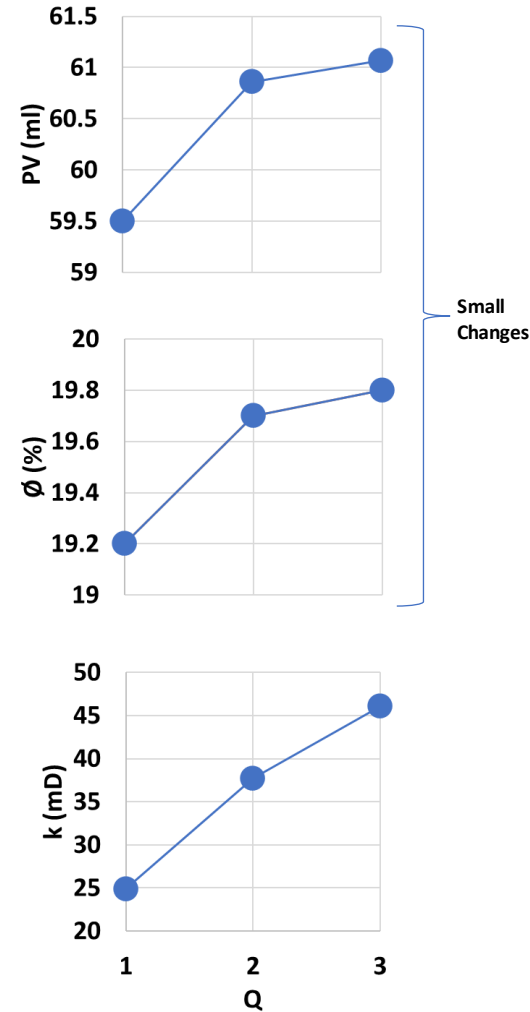
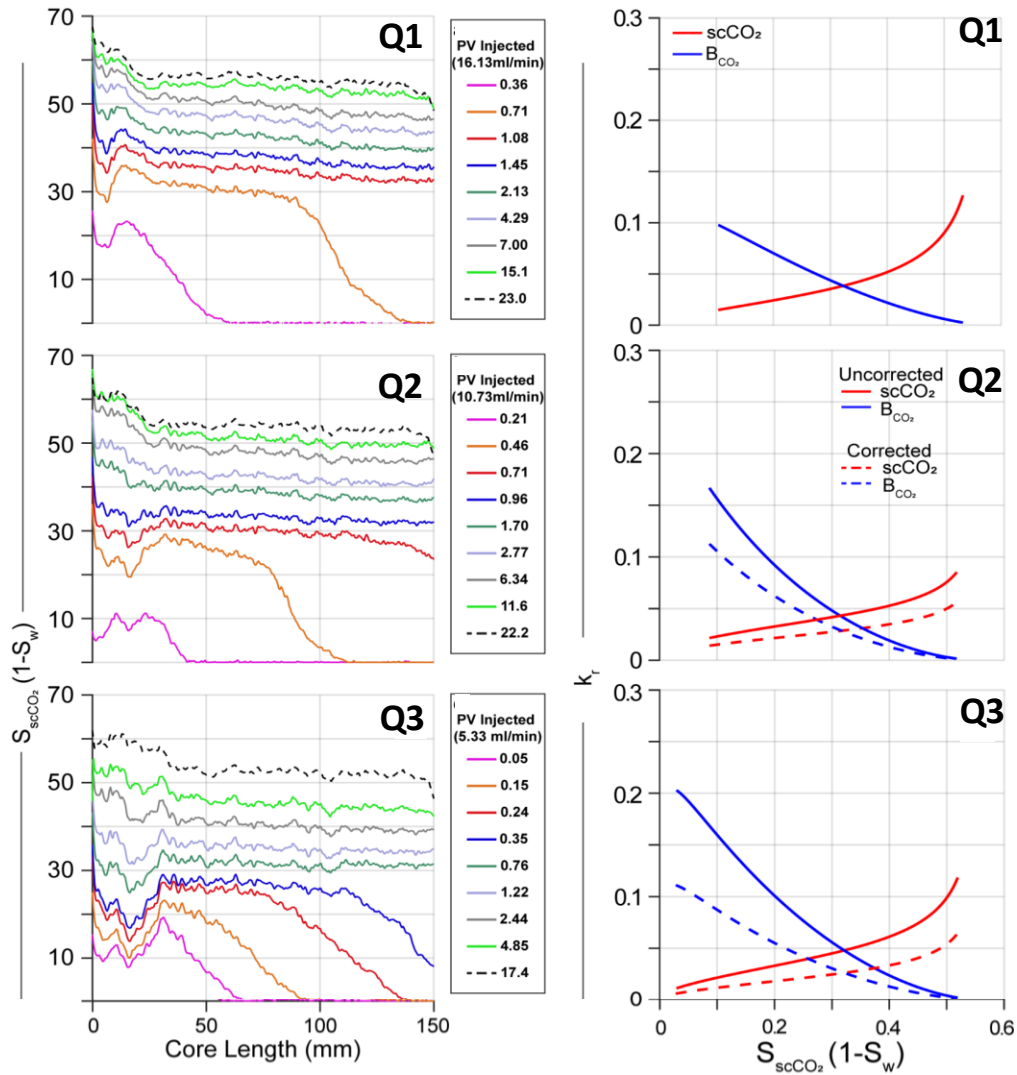


Reactive kr – Methodology Modification

- As dissolution occurs, two physical changes happen:
 - \emptyset/PV both increase
 - k increases, dependent upon connectivity of new dissolution features
- In general, small pores are difficult to isolate in systems that obtain 3D tomographies quickly (order of seconds)
 - Luckily, wormholes are quite large comparably to the resolution of the scanner and easy to isolate.
 - Ilastik used to isolate pores and imagej® for image modification
- The resaturation of the pore space with **brine** after each **scCO₂** flood allows for the determination of k between each test
- Increase in fluid flow pathways, ‘super-highways’, resulted in a drastic changes in k , but only moderate changes in \emptyset/PV



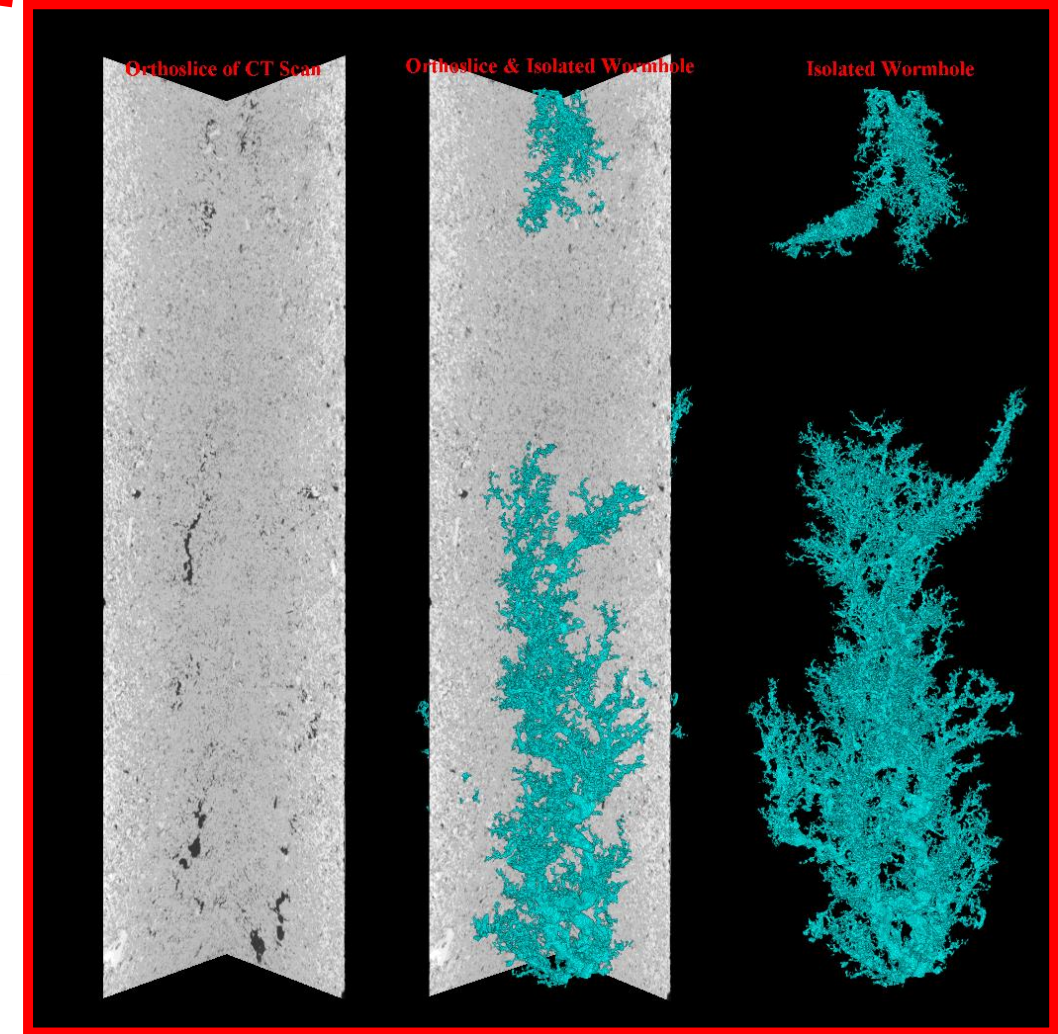
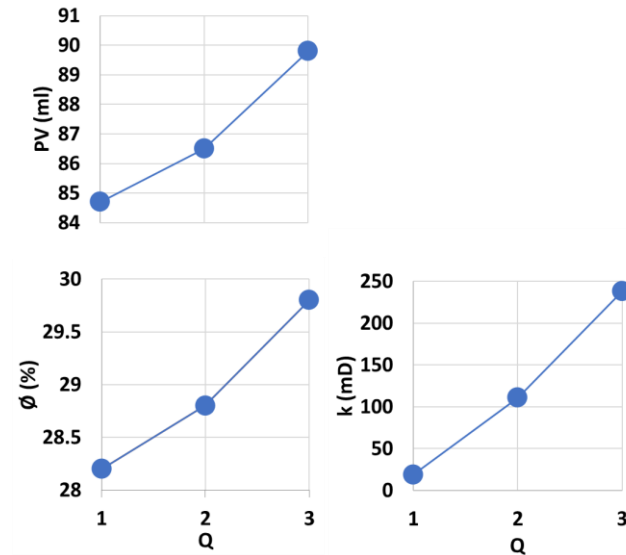
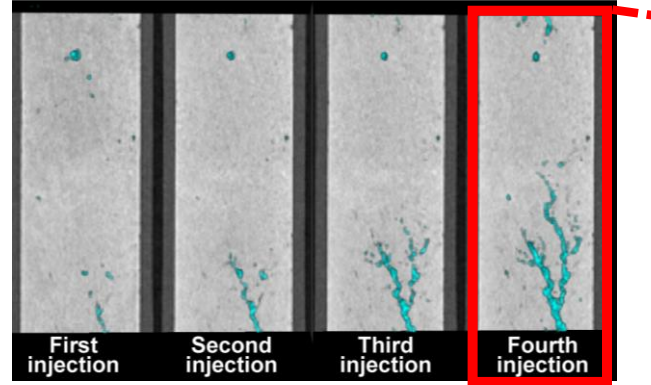
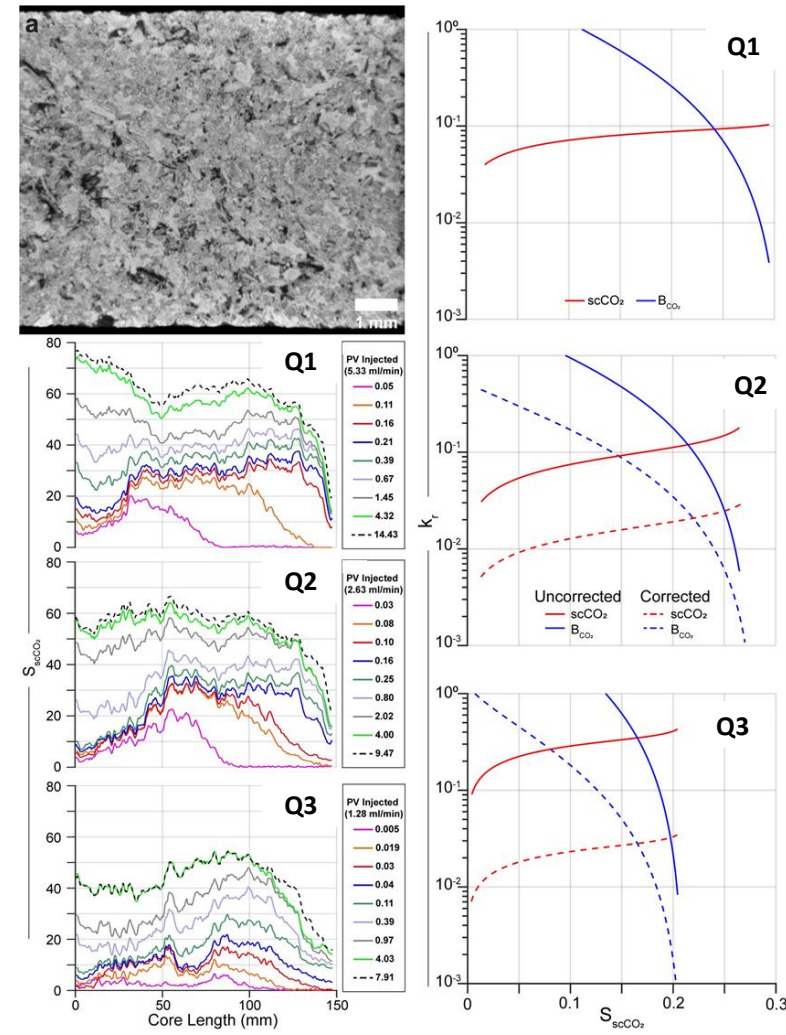
Reactive kr – Reactive Cores, Edwards Yellow



Reactive kr – Reactive Cores, Austin Chalk

Medical CT Scans

Micro-Tomography



Conclusions

1. **It is possible to capture dynamic k_r as a function of dissolution**
 - Time steps, not continuous
2. **Absolute k is the dominant dynamic variable**
 - System transitions from diffuse dominated flow to concentrated flow along primary flow path
3. **K_r shifts and recedes as a function of increased channelization of flow**
 - Cross-over occurs faster and at low $scCO_2$ saturation
 - Potentially less initial occupation of $scCO_2$ if preferential paths are formed

Future Work

1. **Image system at higher resolution during dissolution to capture micro-channels**
2. **Incorporate CFD to determine how channelization proceeds temporally**
3. **Incorporate geochemical modeling to estimate mass transport and determine equilibrium conditions/reactivity**

NETL RESOURCES

VISIT US AT: www.NETL.DOE.gov



@NETL_DOE



@NETL_DOE



@NationalEnergyTechnologyLaboratory



U.S. DEPARTMENT OF
ENERGY