Experimental and Theoretical Study of Water and Solute Transport Mechanisms in Organic-Rich Carbonate Mudrocks*

Anton Padin[1]

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[1] Colorado School of Mines, Golden, CO, USA (anton.padin@gmail.com)

Abstract

The objective of this research is to determine the physicochemical processes underlying water and solute transport in organic-rich source rocks. Experiments were performed on Eagle Ford shale samples composed of organic-rich, low-clay carbonates using a high-pressure triaxial assembly with novel design. Experimental results were successfully matched with a numerical chemical transport model. The mathematical formulation of this model relies on the chemical osmosis principles driving low-salinity brine into high salinity core samples. The results of this research should be beneficial for design of EOR processes in organic-rich shale.

A custom-designed experimental apparatus was constructed to conduct flow tests. The apparatus is capable of maintaining core samples at reservoir pressure, temperature, and confining stress. In addition, a new mathematical model was formulated to simulate flow into the core as a porous medium rather than as a molecule-selective membrane. This new model is based on the following principles: (1) the solvent (low-salinity water) selectively enters the pores by diffusion mass transport and (2) the dissolved salt molecules (which are ionized) are restrained by internal electrostatic forces from diffusing in the opposite direction of the low-salinity brine molecules entering the pore network.

The mathematical model closely matches the experimental results and, more importantly, only very few assumptions were made in matching experiments. For instance, the critical model input data, such as permeability, porosity, and rock compressibility, were obtained from flow experiments on twin cores, and the diffusion coefficient was chosen by history matching. The strengths of the numerical simulation include the following: (1) the mathematical model is based on the mass transport fundamental principles, (2) the model does not require the use of the ambiguously defined membrane efficiency term, and (3) the chemical potential gradient is the reason for the low-salinity brine entering the high-salinity brine cores to generate osmotic pressure within the cores. The latter implies that osmotic pressure is the consequence of water entering the cores, not the cause.

AAPG
Latin America & Caribbean Region

ARGENTINA 2016
Geosciences Technology Workshop
Co-hosted by the Argentine Association of Petroleum Geologists and Geophysicists

Moving toward the Prediction of Unconventional Plays:

Lessons Learned from Tight and Shale Reservoirs in the Neuquén Basin

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Experimental and Theoretical Study of Water and Solute Transport Mechanisms in Organic -Rich Carbonate Mudrocks

Anton Padin, PhD
Colorado School of Mines

Objective

- Determine the physicochemical processes underlying **water and solute transport** in organic-rich **Eagle Ford and Vaca Muerta** source rock samples
- Conduct coupled flow/geomechanical experiments on preserved Eagle Ford shale samples using a **novel high pressure triaxial assembly**
- Include **reservoir conditions**: pressure, temperature and effective stress
- Conduct **transport modeling** to match experiments

Impact

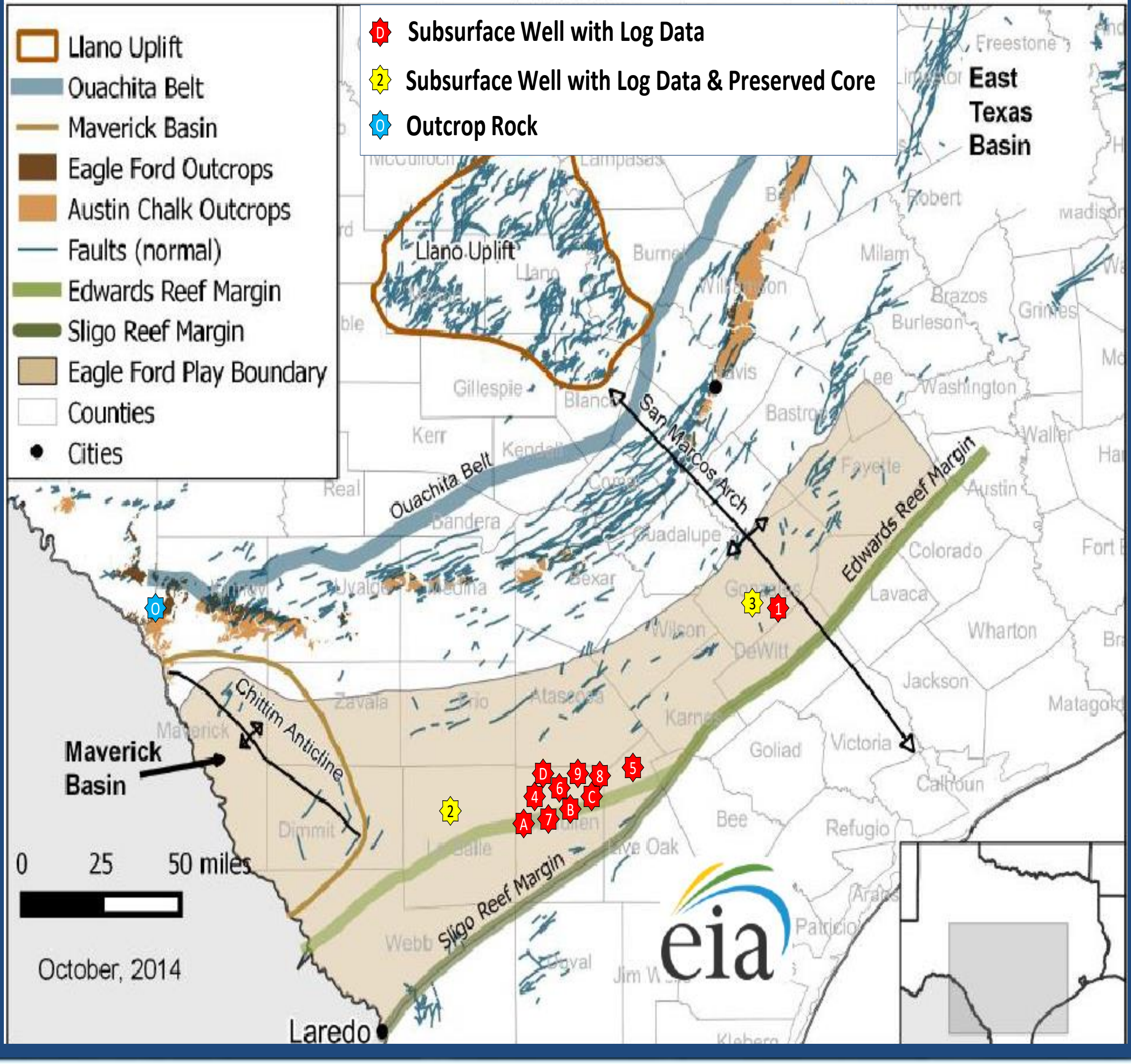
- Use research findings in design of hydraulic fracturing & EOR

Observations from Surveillance of Flowback Water after HF

- Improved production rates after long periods of shut-in
- Variable flowback-water recovery
- Time-dependent, gradual increase in flowback water salinity (Na^+, Ca^{2+}, K^+, Fe, Sr^{2+} or Ba^{2+})

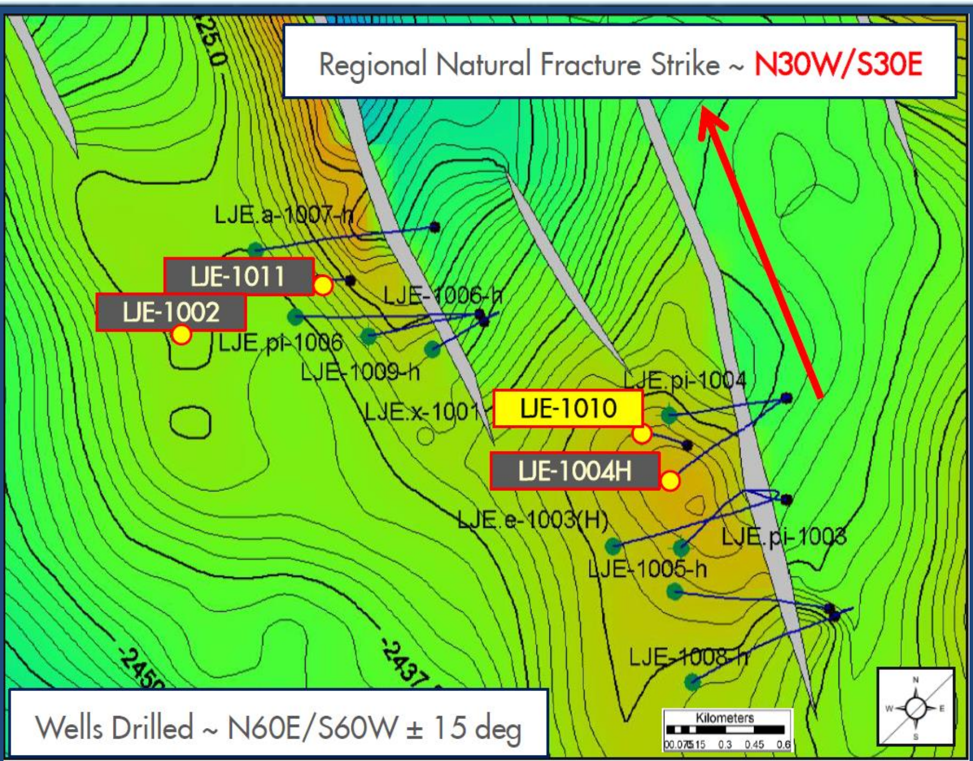
Observations from EOR Field Studies

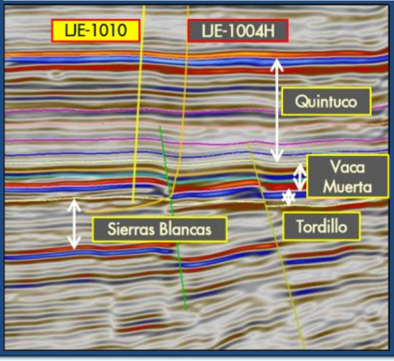
- Improved oil recovery by: Pressure/temperature increase and salinity decrease
- Attributed to wettability changes:
  - Similar to alkaline flooding – interfacial tension reduced
  - Increased repulsion forces, towards more water-wet

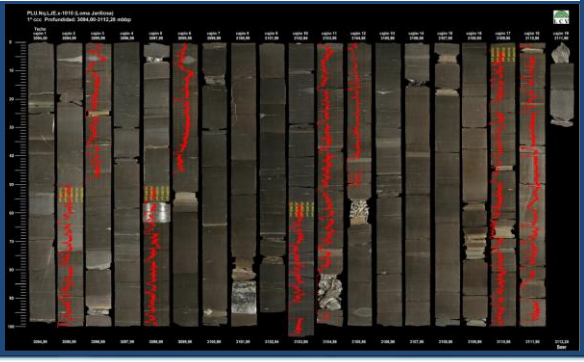


Source Rock I:
Upper Eagle Ford Marl

- ❑ Upper Cretaceous
- ❑ Isolated carbonate platform surrounded by siliciclastics
- ❑ Deposited during a sea level transgression.



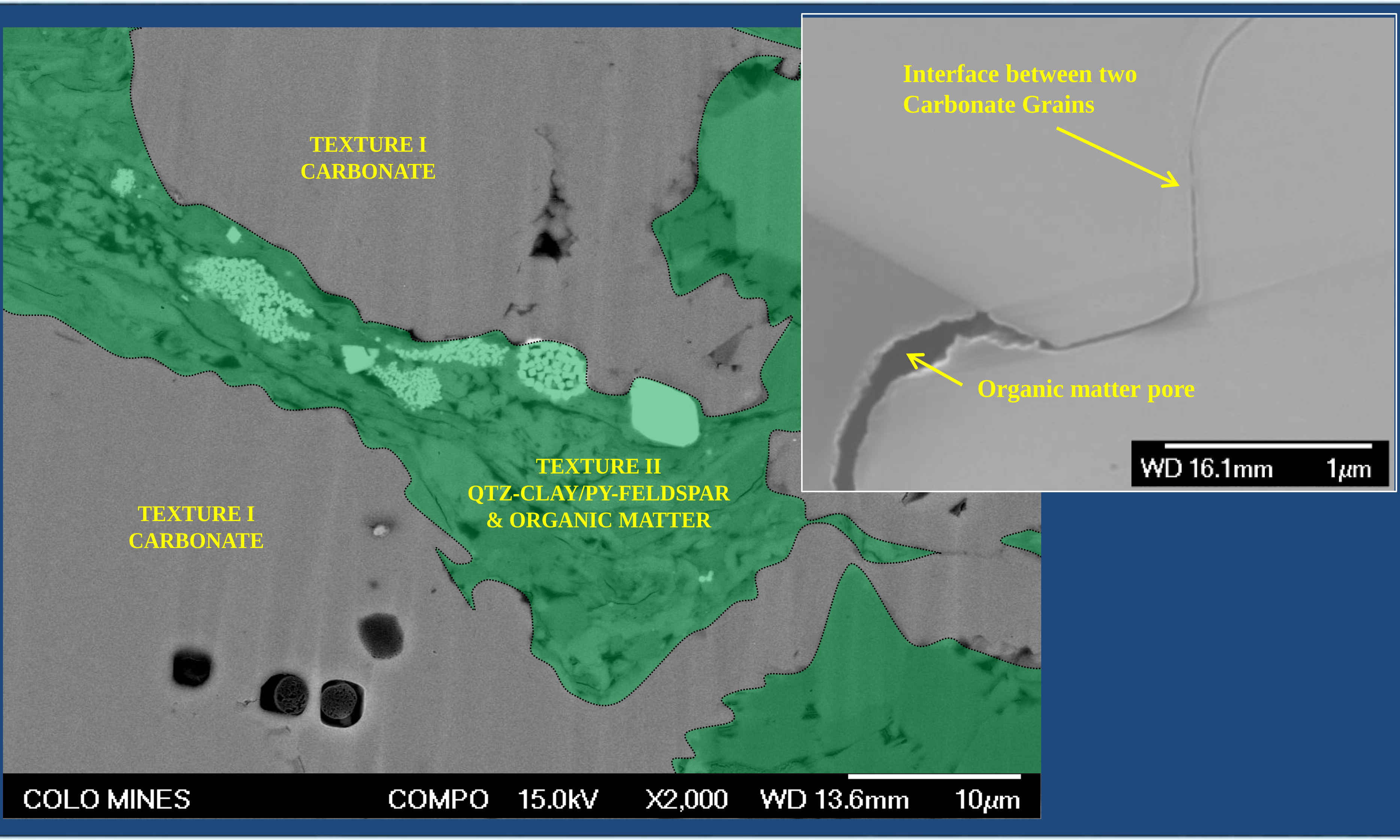




Source Rock II:
Vaca Muerta Marl

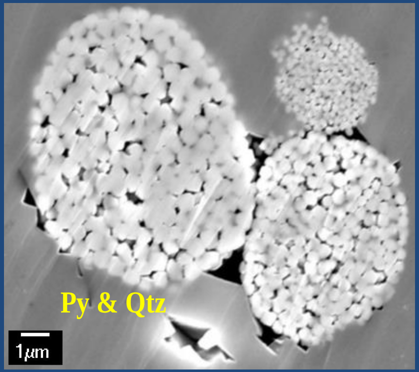
- ❑ Marine, black to dark brown organic-rich mudstone
- ❑ High contents of TOC, hydrogen index and anomalous concentrations of molybdenum, vanadium, nickel and chromium
- ❑ Core from the lower Vaca Muerta, well LJE-1010

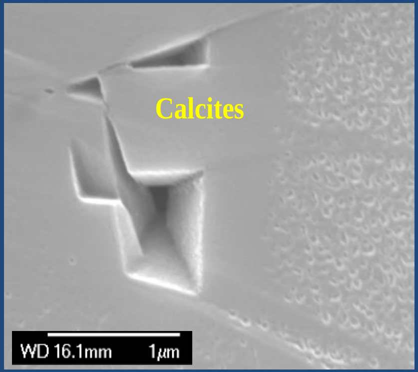
Sample Core: Texture Interface and Microfractures

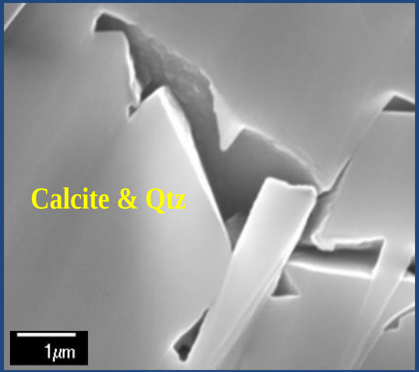


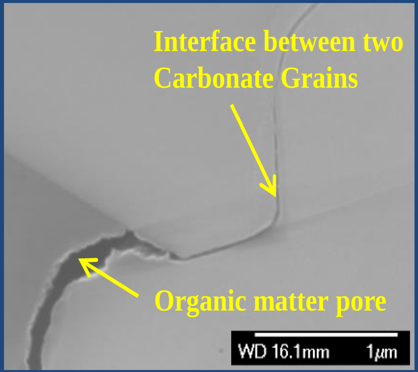
Inorganic Pore Types

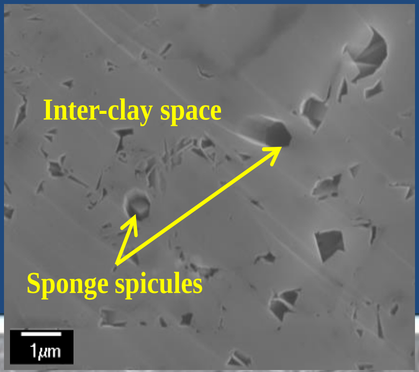
Interparticle Pores

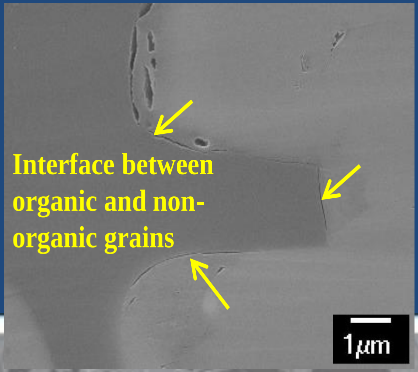




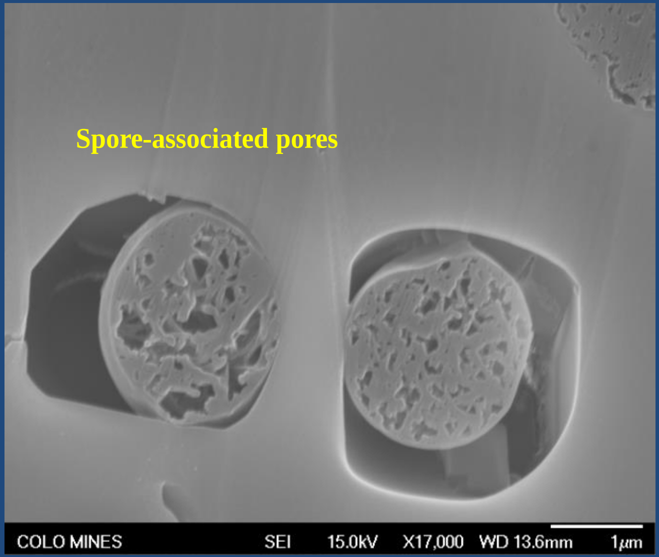


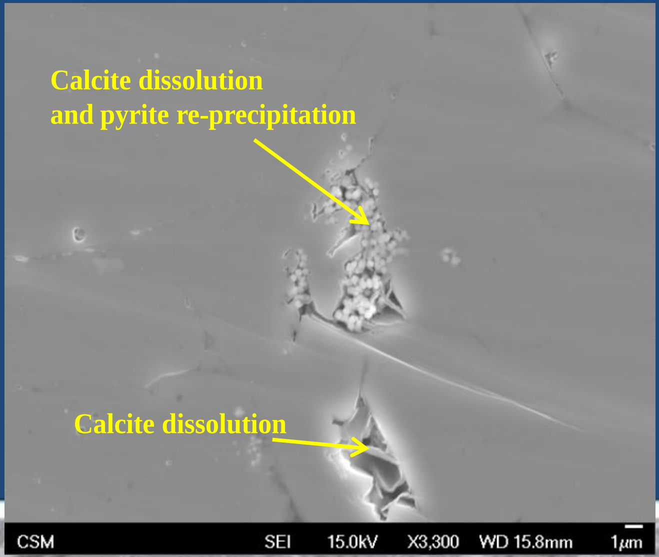






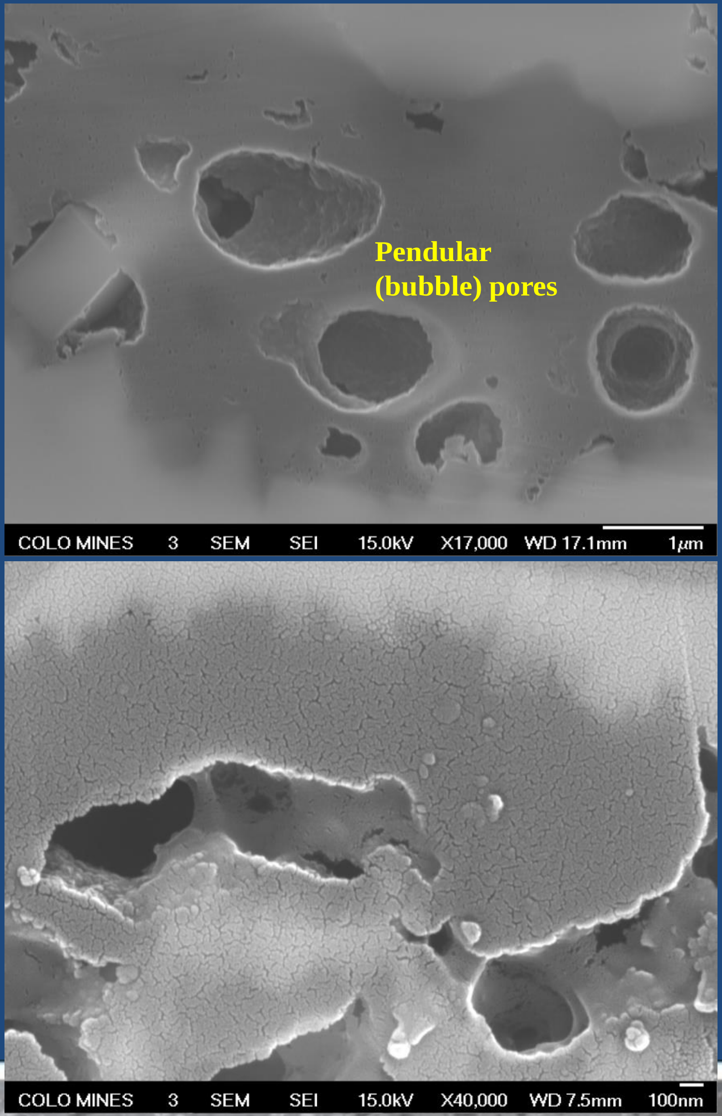
Intraparticle Pores



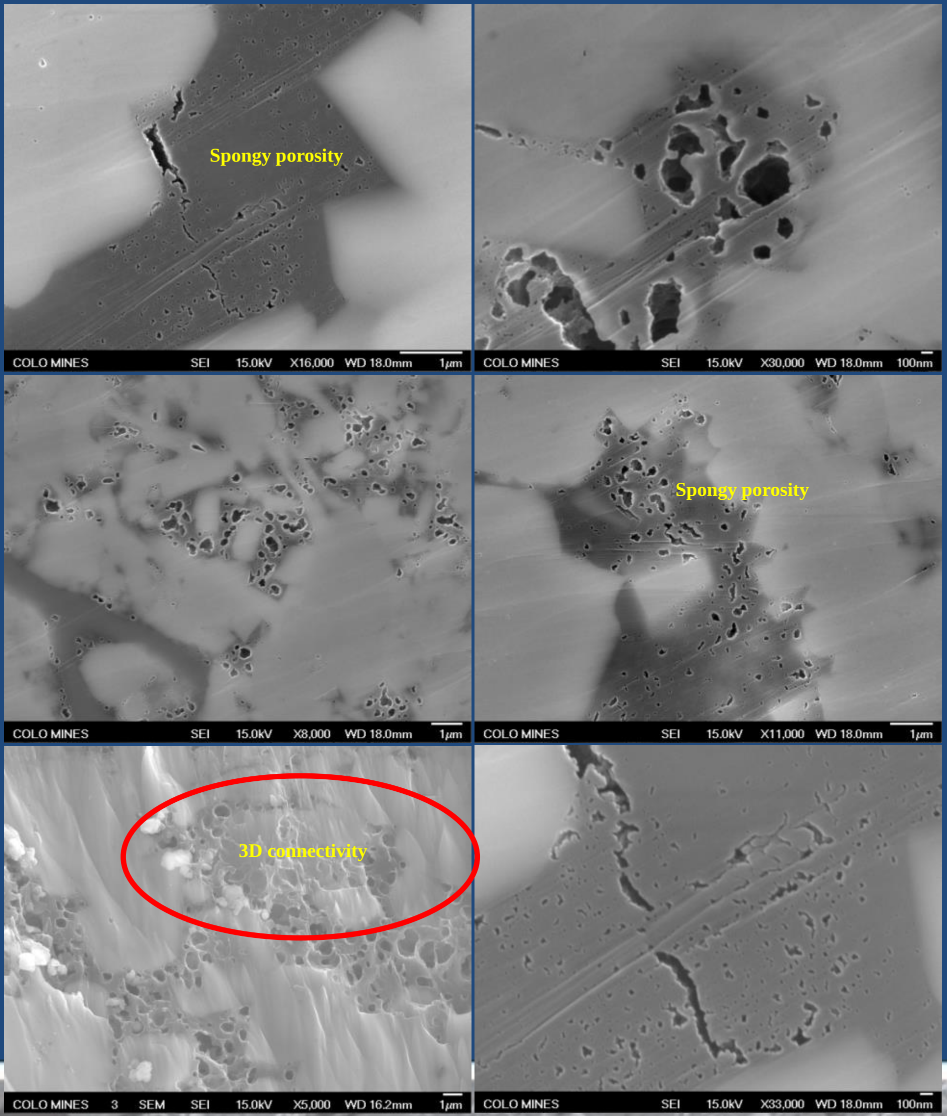


Organic Pore Types

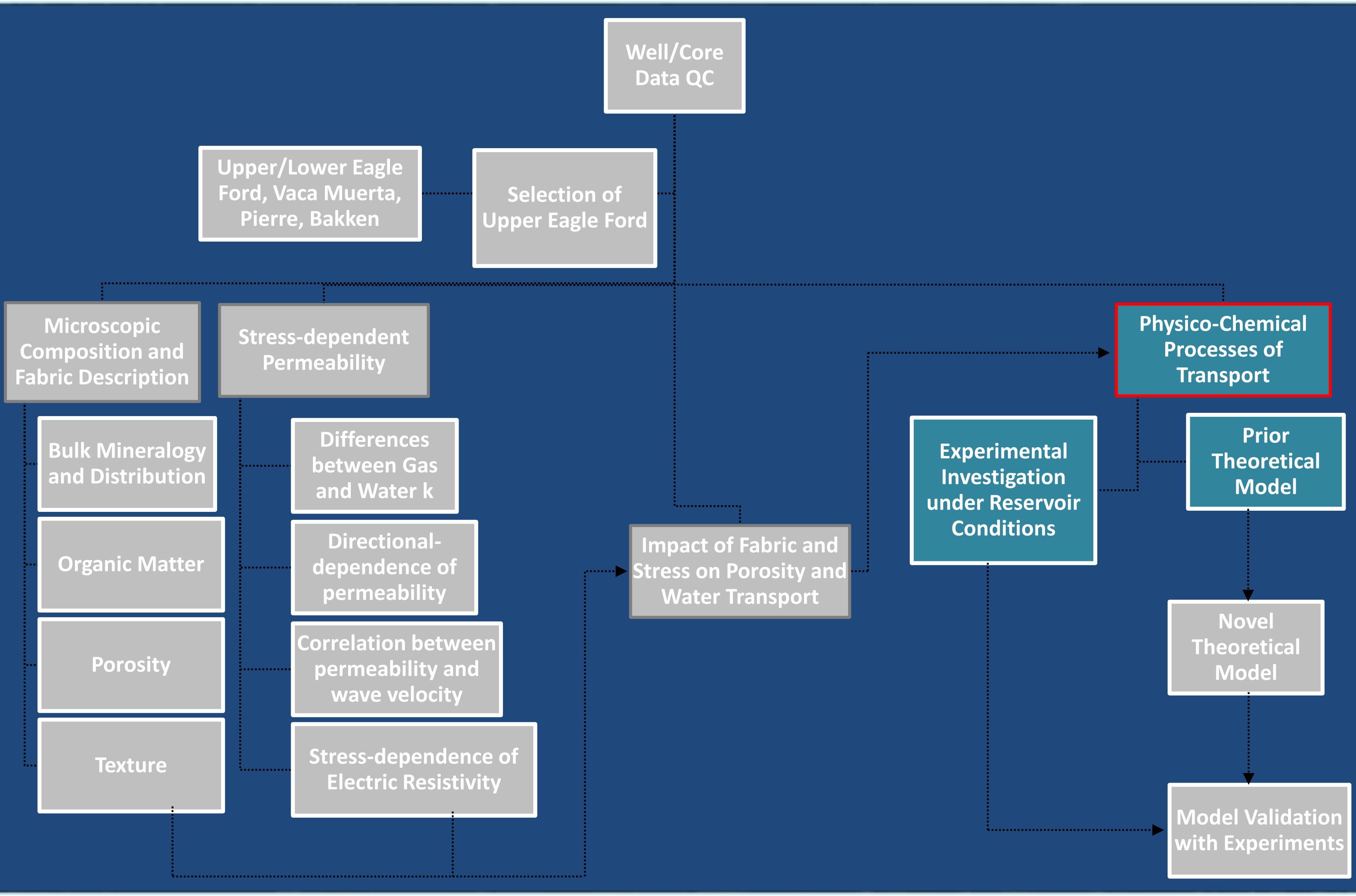
Pendular (Bubble) Pores



Spongy Porosity



Experiments on Solute/Water Transport in Mudrocks



Well/Core Data QC

Upper/Lower Eagle Ford, Vaca Muerta, Pierre, Bakken

Selection of Upper Eagle Ford

Microscopic Composition and Fabric Description

- Bulk Mineralogy and Distribution
- Organic Matter
- Porosity
- Texture

Stress-dependent Permeability

- Differences between Gas and Water k
- Directional-dependence of permeability
- Correlation between permeability and wave velocity
- Stress-dependence of Electric Resistivity

Impact of Fabric and Stress on Porosity and Water Transport

Physico-Chemical Processes of Transport

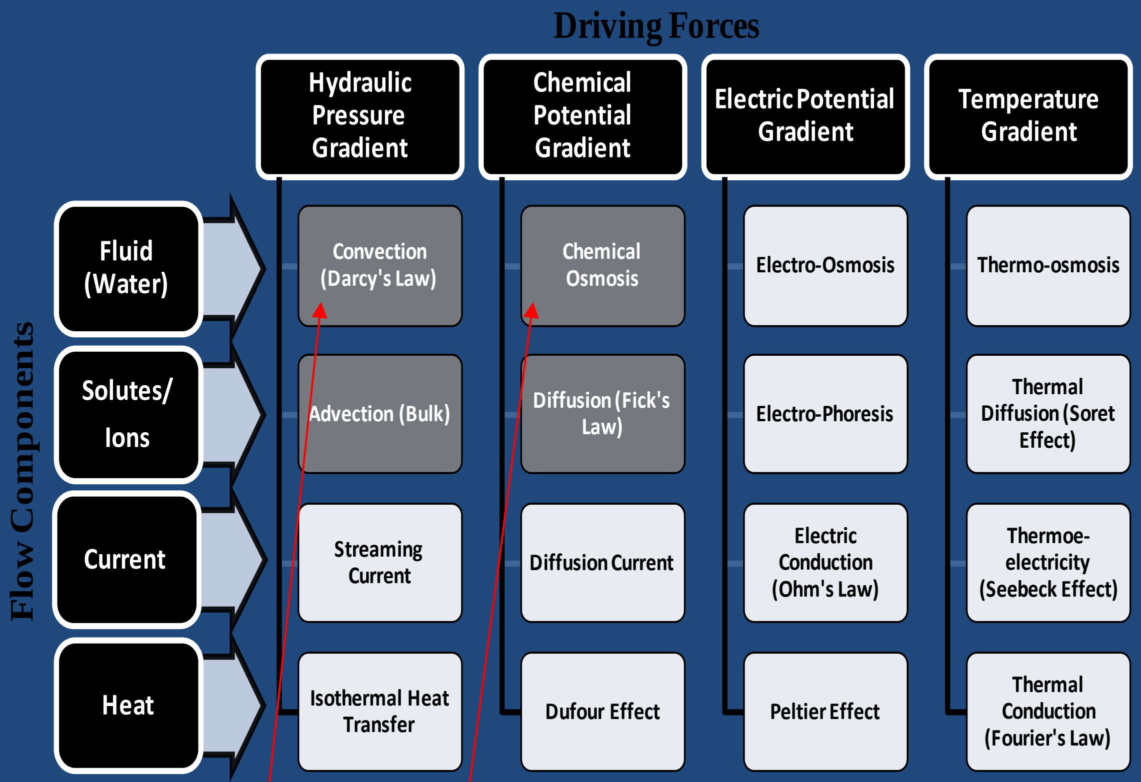
Experimental Investigation under Reservoir Conditions

Prior Theoretical Model

Novel Theoretical Model

Model Validation with Experiments

Transport Laws in Mudrocks



Driving Forces

Flow Components

	Hydraulic Pressure Gradient	Chemical Potential Gradient	Electric Potential Gradient	Temperature Gradient
Fluid (Water)	Convection (Darcy's Law)	Chemical Osmosis	Electro-Osmosis	Thermo-osmosis
Solutes/ Ions	Advection (Bulk)	Diffusion (Fick's Law)	Electro-Phoresis	Thermal Diffusion (Soret Effect)
Current	Streaming Current	Diffusion Current	Electric Conduction (Ohm's Law)	Thermoe-electricity (Seebeck Effect)
Heat	Isothermal Heat Transfer	Dufour Effect	Peltier Effect	Thermal Conduction (Fourier's Law)

$$\nabla \cdot \left[\rho_w \frac{k}{\mu} \left(\nabla p - E_{op} \nabla \pi \right) \right] + \rho_w \hat{q}_w = \frac{\partial}{\partial t}\left(\rho_w \phi \right)$$

- E_{op} **empirical scaling factor** termed ***membrane efficiency***
- Defines the selectivity of membrane to specific ions
- Not-well-defined physical entity

$$E_{op} = 1 - \frac{a_{solute}}{a_{water}}$$

- E_{op} depends on the ion type:

  $KCl < NaCl < CaCl_2 < MgCl_2$
- $E_{op} = 0$ if $k > 0.2$ nD

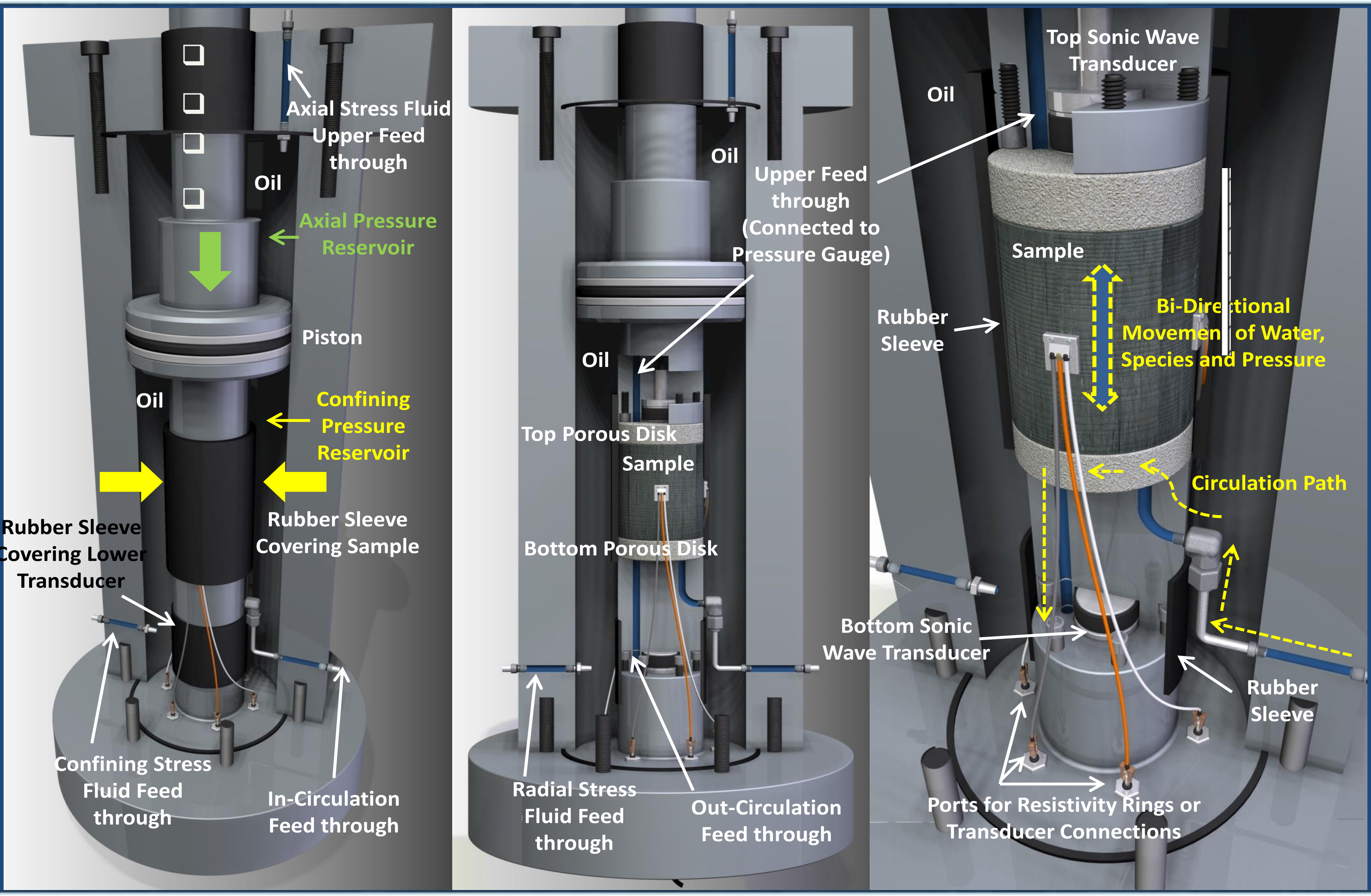
Gaps from prior research in surface-fluid interaction

- ❑ Most research focused on: clay-rich, non-organic, seal shales
- ❑ In seal shales – interactions clay surface-water-solute are dominant
- ❑ No reservoir conditions (P,T) in experiments

Our set of tests

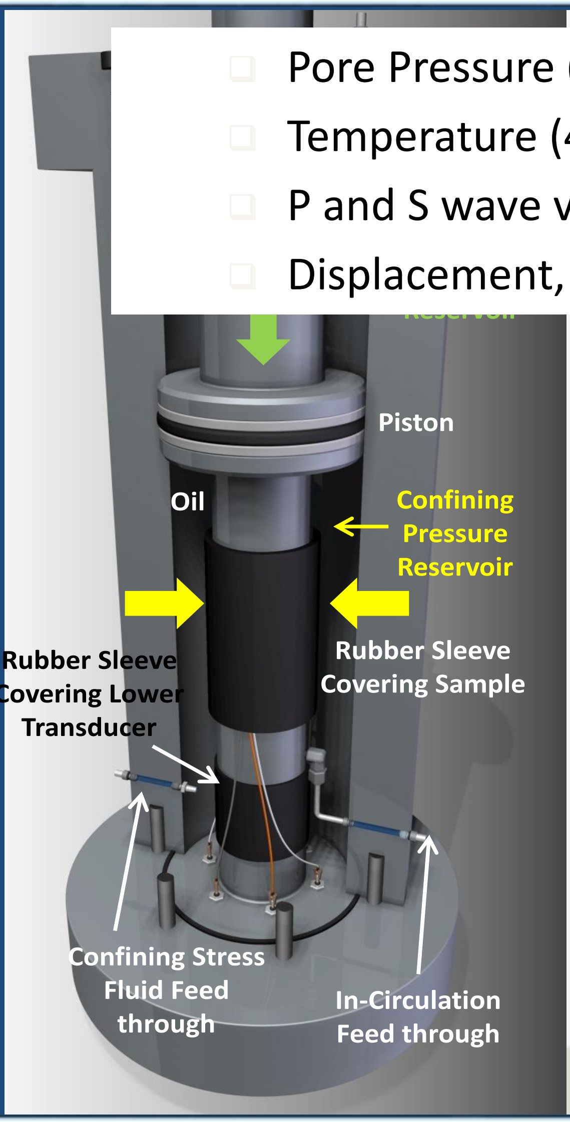
- ❑ Conducted at reservoir conditions (6,000 psi conf., 4,000 psi Pp)
- ❑ Studied impact of solute type (monovalent, Na+ and K+, and divalent, Ca2+) on surface-fluid interaction
- ❑ Impact of initial saturation, effective stress and solute concentration

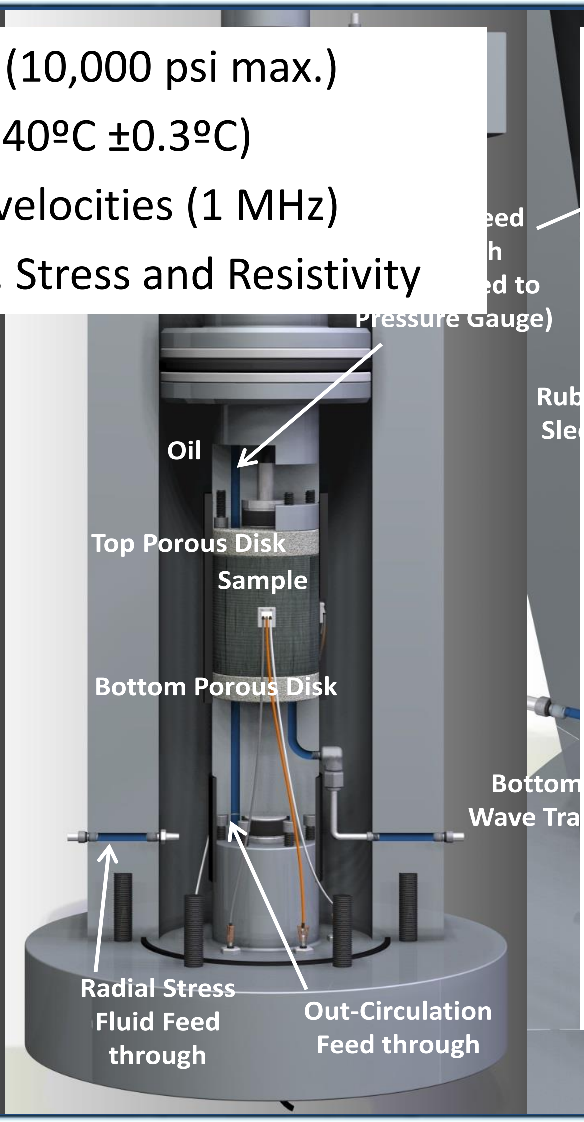
Permeability-Osmosis Apparatus – Reservoir Conditions

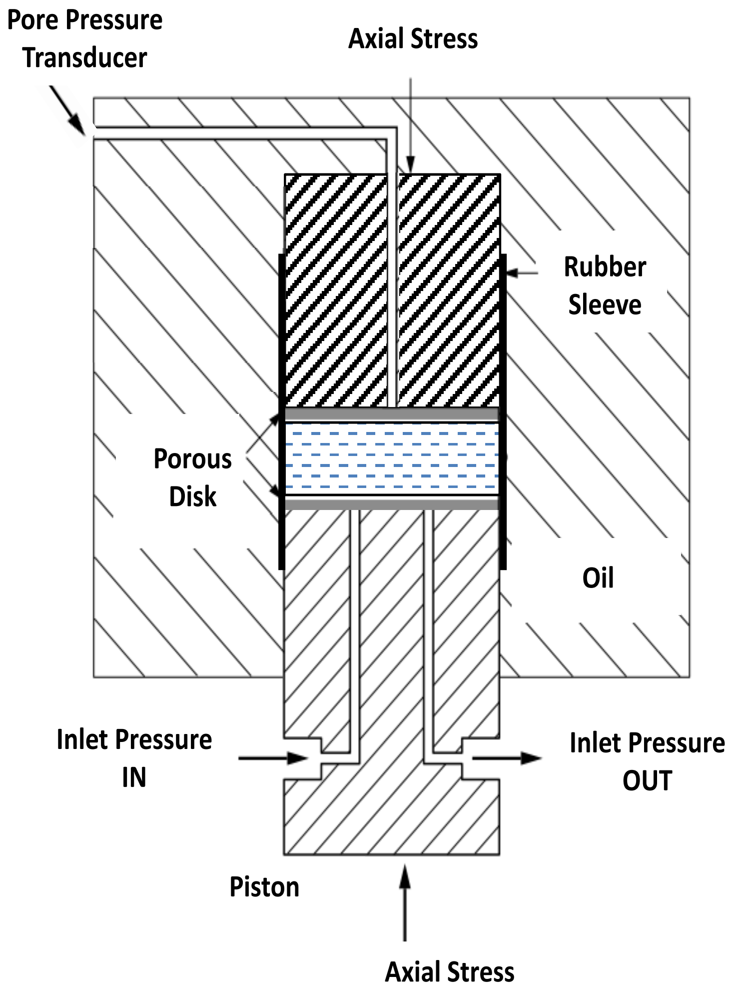


Permeability-Osmosis Apparatus – Reservoir Conditions

- Pore Pressure (10,000 psi max.)
- Temperature (40ºC ±0.3ºC)
- P and S wave velocities (1 MHz)
- Displacement, Stress and Resistivity

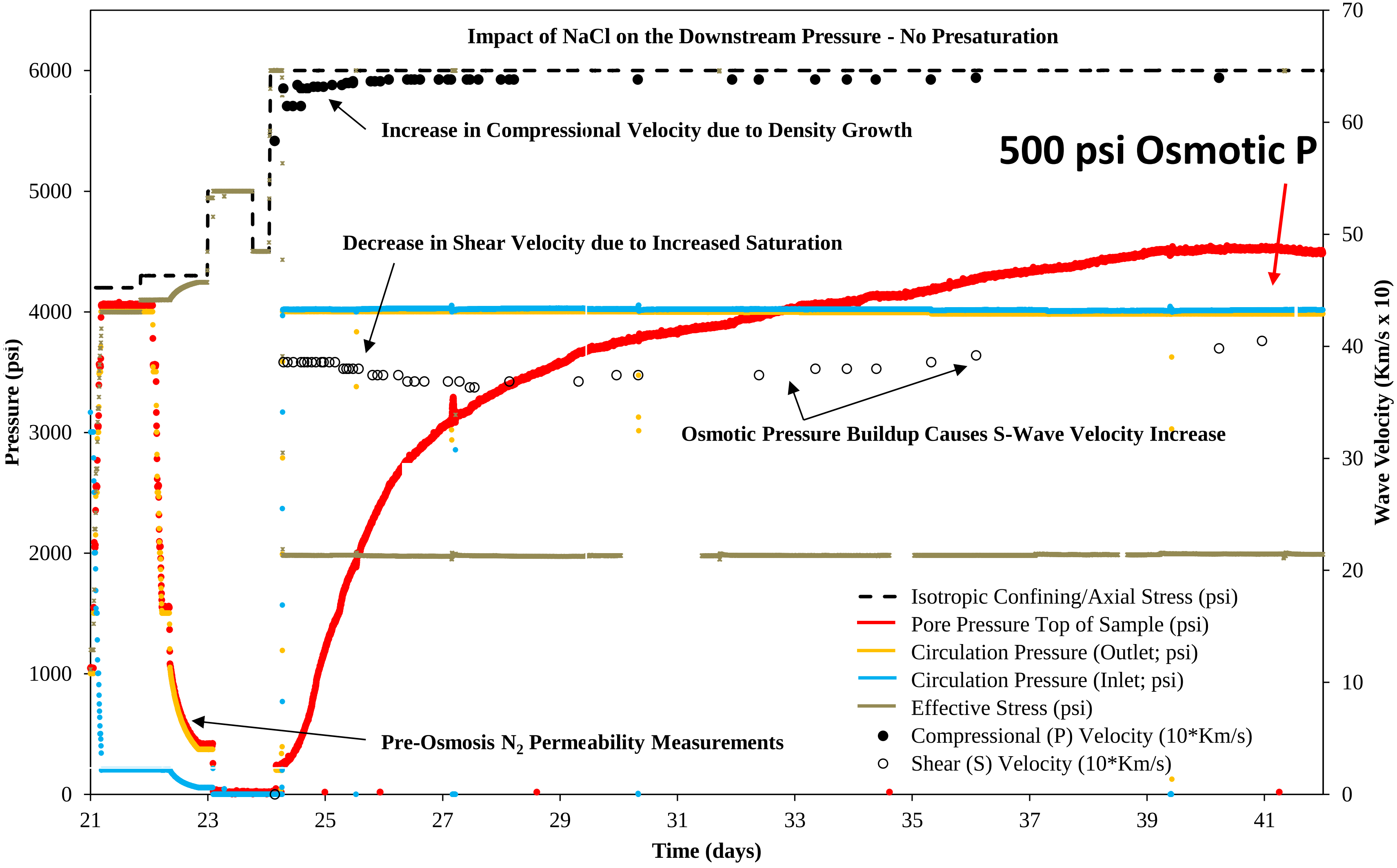






Transducer Connections

Impact of Solute Type - NaCl 1,000 ppm



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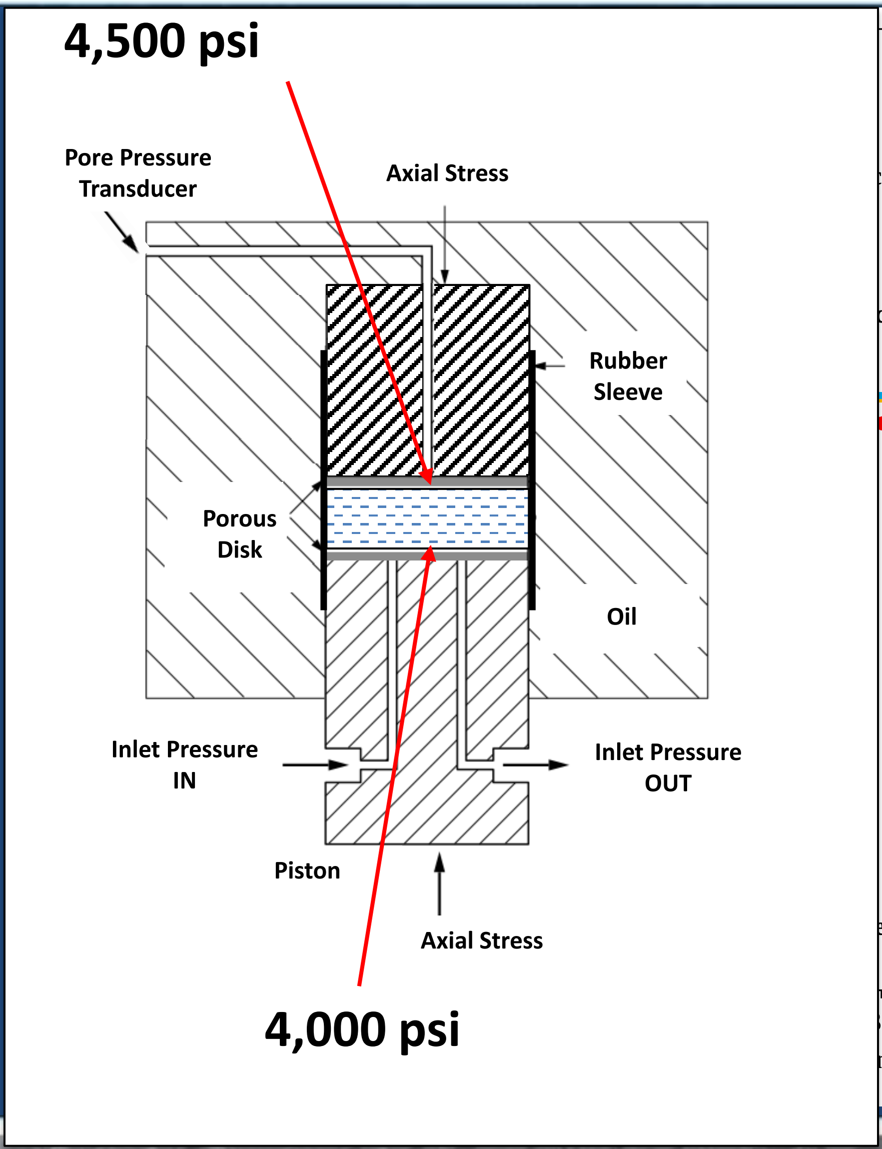
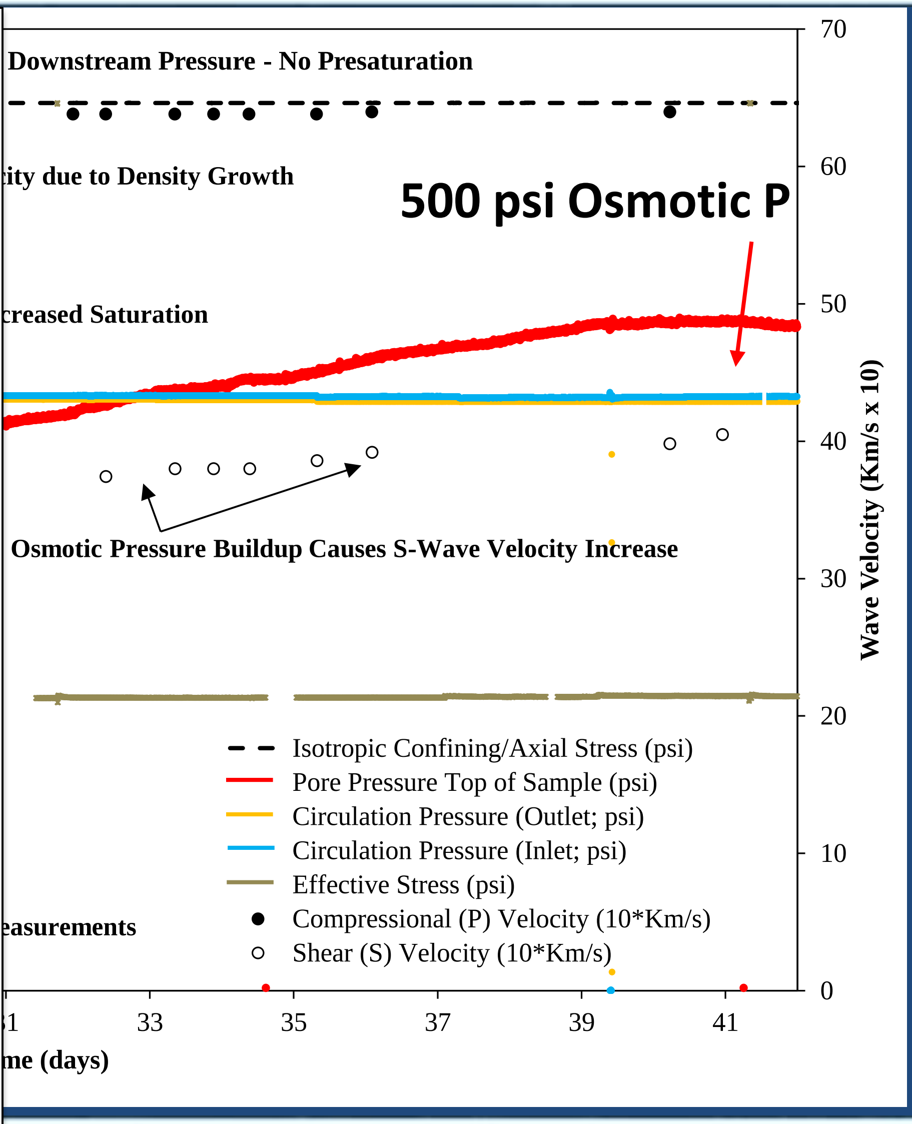


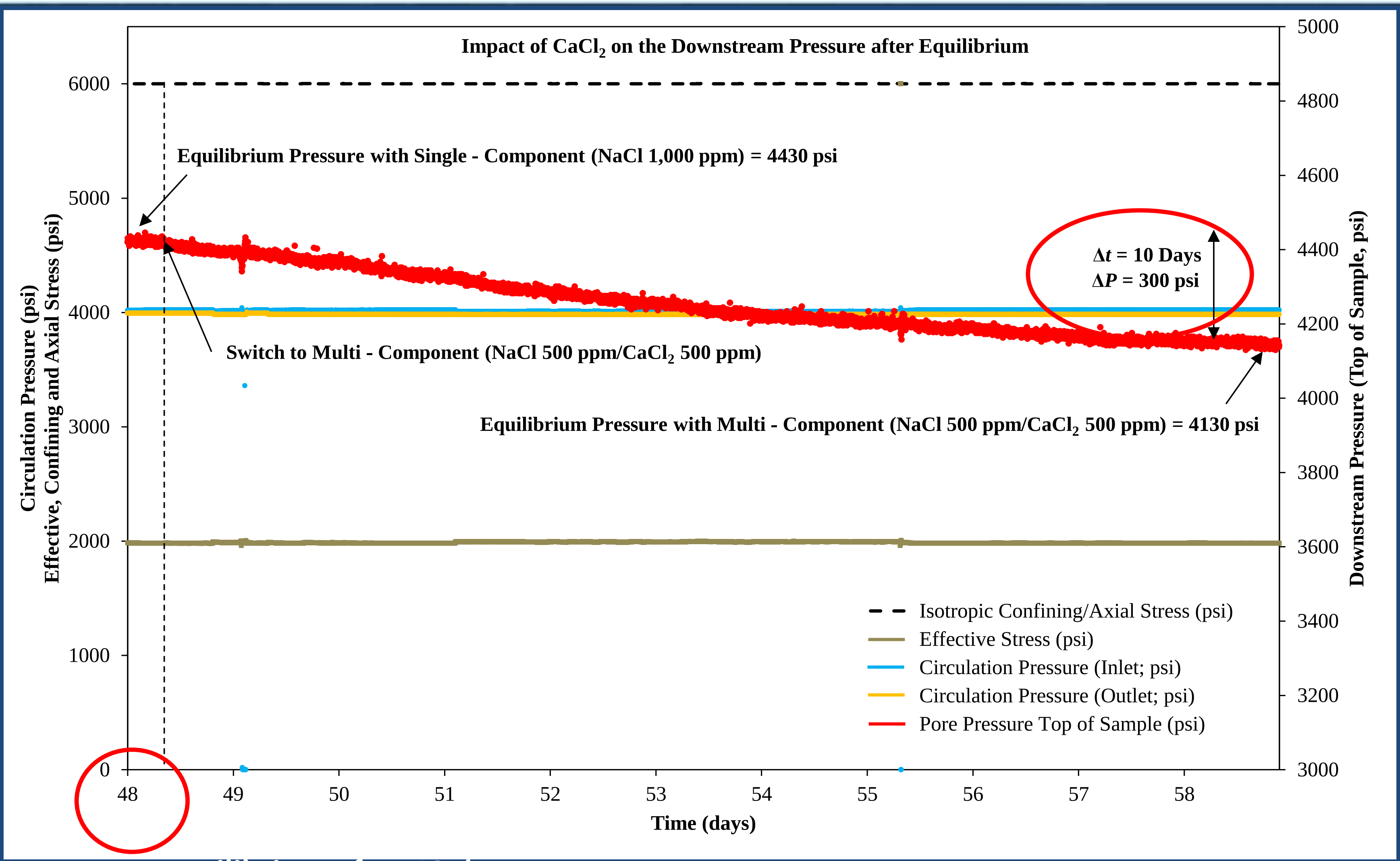
4,500 psi

4,000 psi



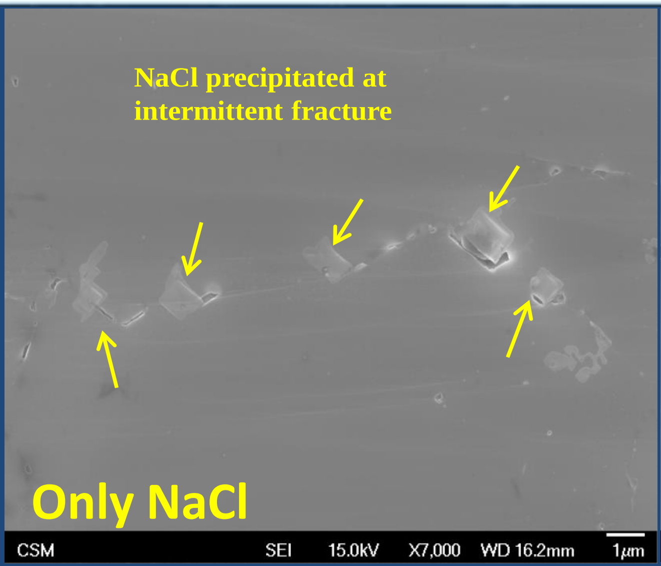
500 psi Osmotic P

Impact of Solute Type – Replacing low salinity NaCl by $CaCl_2$



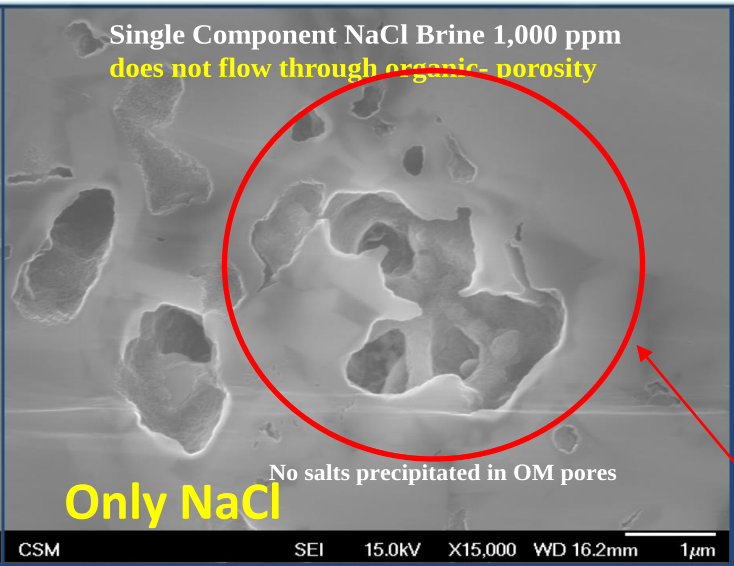
Equilibrium after 48 days

When we add CaCl$_2$, NaCl diffuses through organic porosity



NaCl precipitated at intermittent fracture

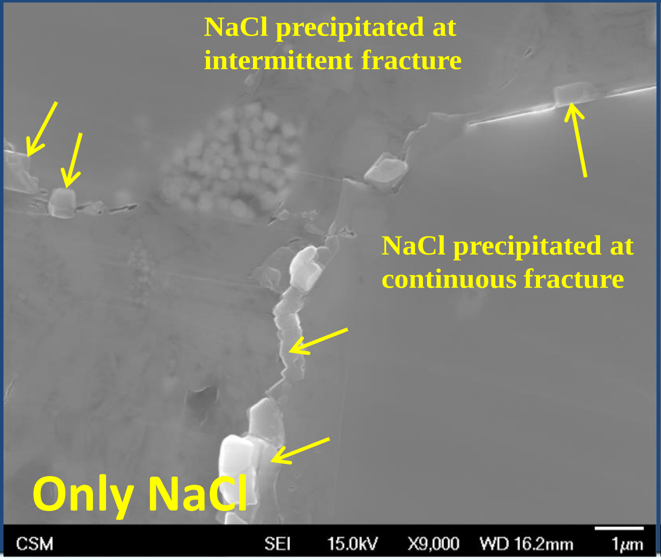
Only NaCl



Single Component NaCl Brine 1,000 ppm does not flow through organic- porosity

No salts precipitated in OM pores

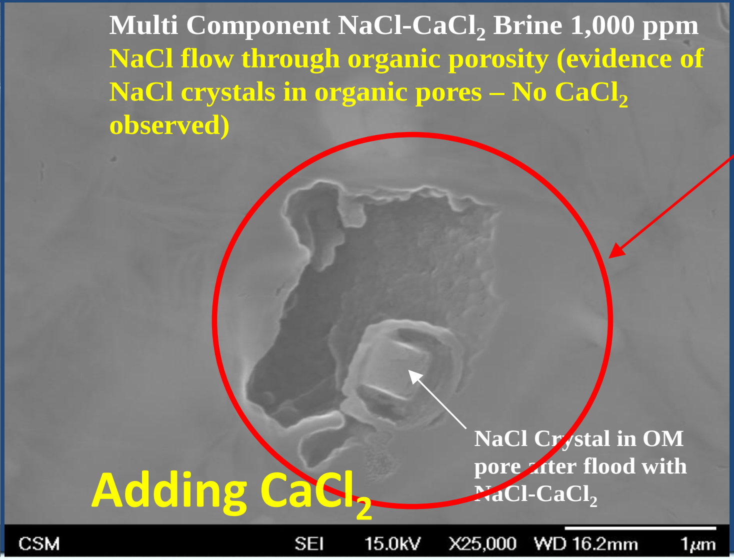
Only NaCl



NaCl precipitated at intermittent fracture

NaCl precipitated at continuous fracture

Only NaCl



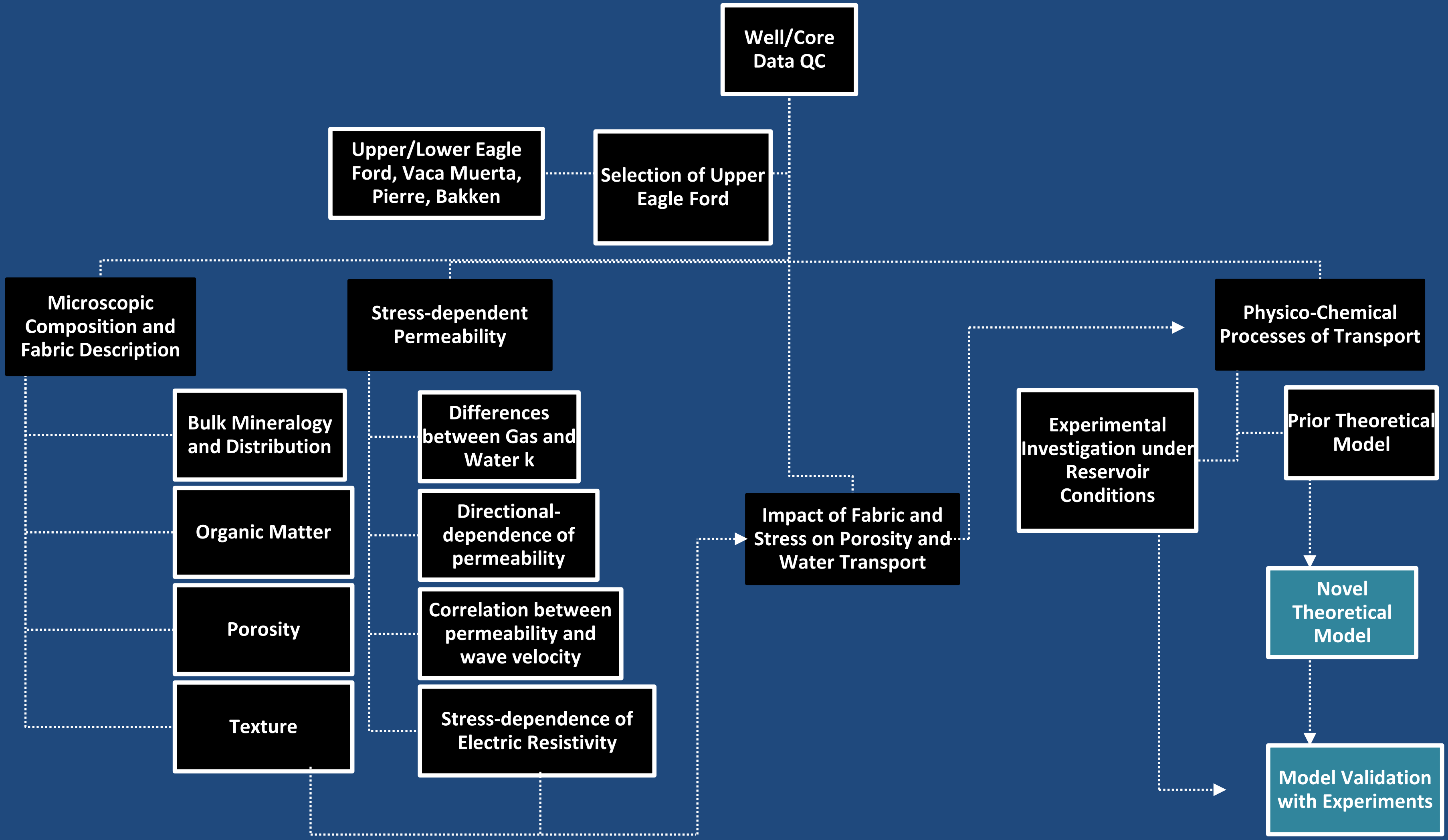
Multi Component NaCl-CaCl$_2$ Brine 1,000 ppm NaCl flow through organic porosity (evidence of NaCl crystals in organic pores – No CaCl$_2$ observed)

NaCl Crystal in OM pore after flood with NaCl-CaCl$_2$

Adding CaCl$_2$

Vs.

Novel Conceptual Approach to Transport Mechanisms



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Impact of Fabric and Stress on Porosity and Water Transport

Physico-Chemical Processes of Transport

Experimental Investigation under Reservoir Conditions

Prior Theoretical Model

Novel Theoretical Model

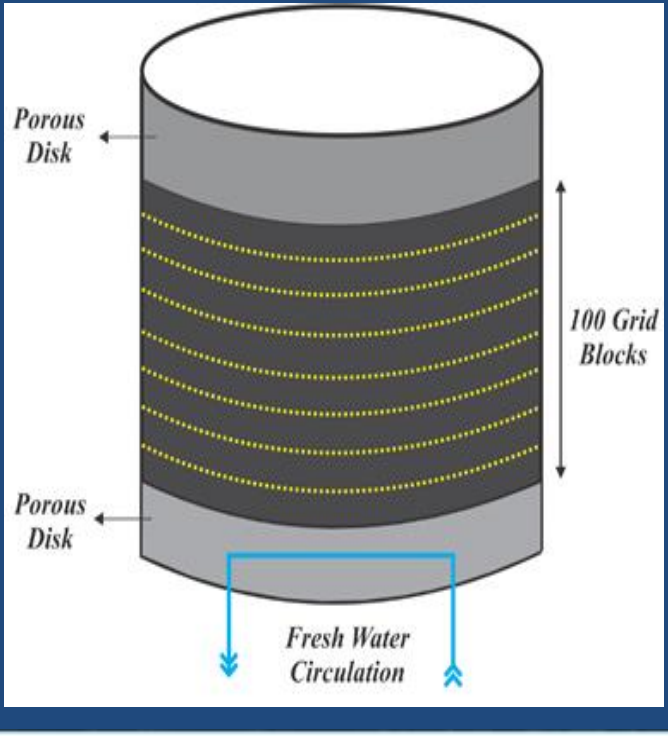
Model Validation with Experiments

Existing Mathematical Model has Critical Limitations

- ❑ Rock assumed a semi-permeable membrane, but thickness much larger than a membrane
- ❑ Osmotic pressure considered the imbibing force

We treat porous media as nano-tubes rather than a membrane

- ❑ **Osmotic pressure** is the **consequence** of the selective molecular transport by the solvent, **not the imbibing force**
- ❑ Only H_2O allowed to enter the pore space
- ❑ Salt molecules are restrained by internal forces to move against water molecule flow
- ❑ Water and solvent flow inside core both by advective flow and molecular diffusion



Fundamental equations:

- Component 1 (solute)

$$\frac{\partial}{\partial x}\left[\rho D_{1,2}^{eff}\frac{\partial C_1}{\partial x}+\rho C_1\frac{k}{\mu}\frac{\partial p}{\partial x}\right]=\frac{\partial}{\partial t}\left(\phi\rho C_1\right)$$

Solute diffusion *Bulk solute advection*

- System of three equations with three primary variables
- Solved for pore pressure *p*, water and solute concentrations (C_2 and C_1)

- Component 2 (water)

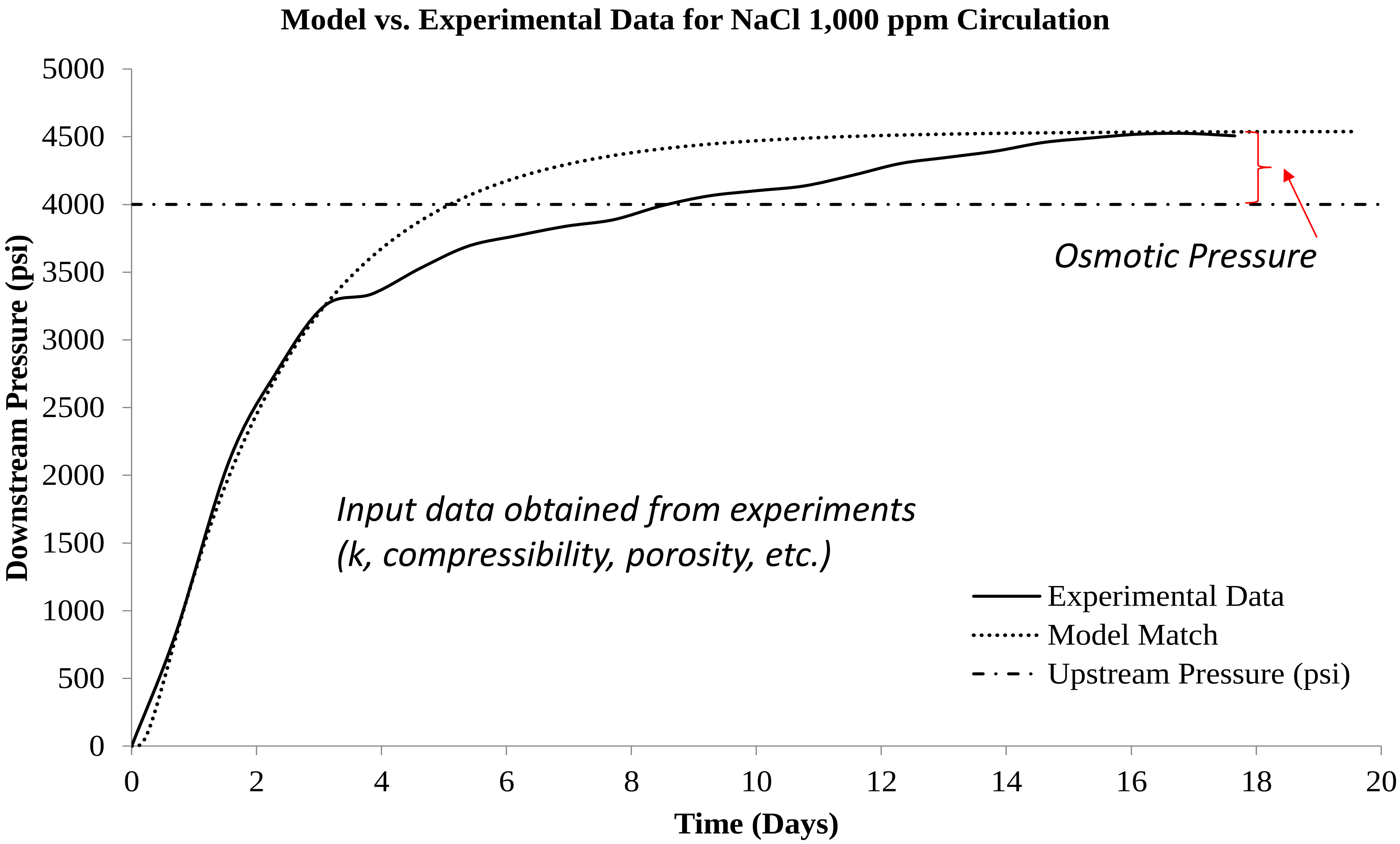
$$\frac{\partial}{\partial x}\left[\rho D_{2,1}^{eff}\frac{\partial C_2}{\partial x}+\rho C_2\frac{k}{\mu}\frac{\partial p}{\partial x}\right]+\left\{\begin{array}{l}\left[\dfrac{\rho D_{eff}\left(C_2^{*}-C_{2,1}\right)}{\frac{\left(\Delta x\right)^2}{2}}\right]\delta\left(x-x_1\right)\\ -\left[\dfrac{\rho\frac{k}{\mu}C_2\left(p_1^{n+1}-p_{in}^{*}\right)}{\frac{\left(\Delta x\right)^2}{2}}\right]\delta\left(x-x_1\right)\end{array}\right\}=\frac{\partial}{\partial t}\left(\phi\rho C_2\right)$$

$$C_1+C_2=1$$

Water diffusion due to chemical osmosis

Water advection

Boundary conditions



Osmotic Pressure

Input data obtained from experiments (k, compressibility, porosity, etc.)

Advantages over Prior Models

- ☐ Simpler formulation based on transport phenomena
- ☐ No empirical scaling factor
- ☐ Water imbibes because of selective molecular transport by the solvent
- ☐ No thermodynamic **activity** is needed for transport equations
- ☐ Diffusion coefficient is a more fundamental parameter than membrane efficiency
- ☐ Impact of ions other than Na+ and Cl- can be modeled using additional components

Limitations

- ☐ Not capturing electro-osmosis (important for high (>50%)-clay content shales)
- ☐ Not capturing impact of organic-matter surface forces