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Fundamental Understanding of CH_4-CO_2-H_2O Interactions in Shale Nanopores under Reservoir Conditions

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management and Natural Gas & Oil Research Project Review Meeting

Virtual Meetings August 2 through August 31, 2021

Team

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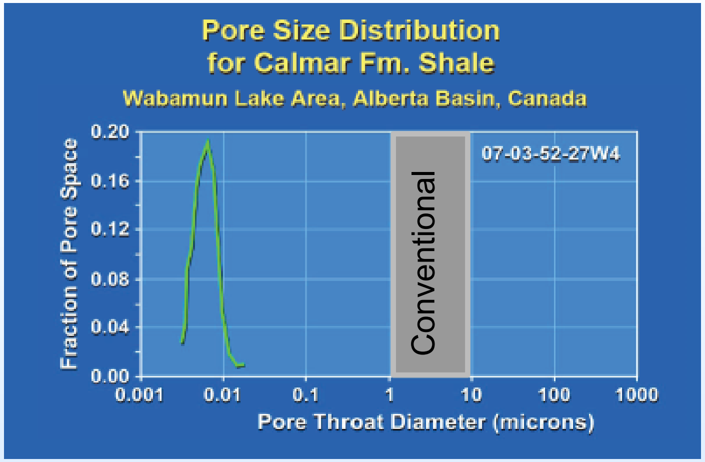
- Shikha Sharma (West Virginia University)
- Bruce Brown (DOE Manager)

Presentation Outline

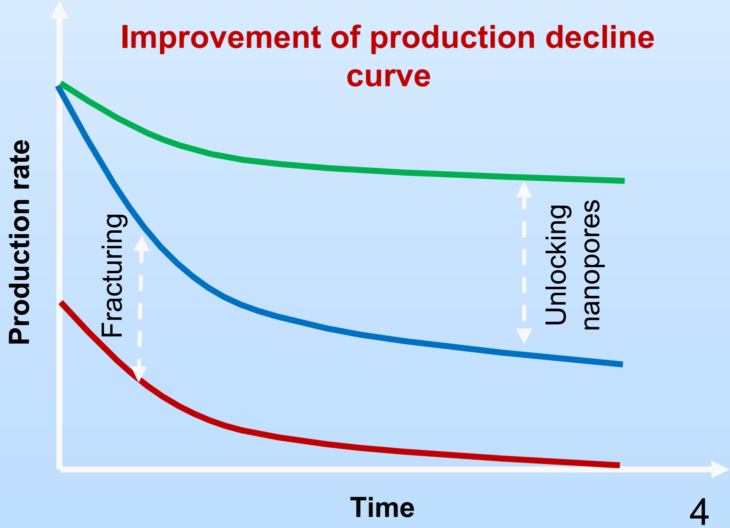
- Goal
- Accomplishments to date
- Technical Status
- Summary & Benefit to the Program
- Lesson Learned

Goals and Objectives

- **Unconventional reservoir: What makes it unconventional?**
  - Nanopores (~1 - 100 nm) accounts for > 90% of total porosity in shale.
  - Fluids confined in nanopores behave drastically differently from their bulk phases (Wang, 2014, Chem. Geol.).
- **Objectives:**
  - Understand fluid (CH_4-CO_2-H_2O) behaviors in shale nanopores;
  - Explore possibilities to unlock these nanopores to improve wellbore production.



Bachu & Bennion (2006)

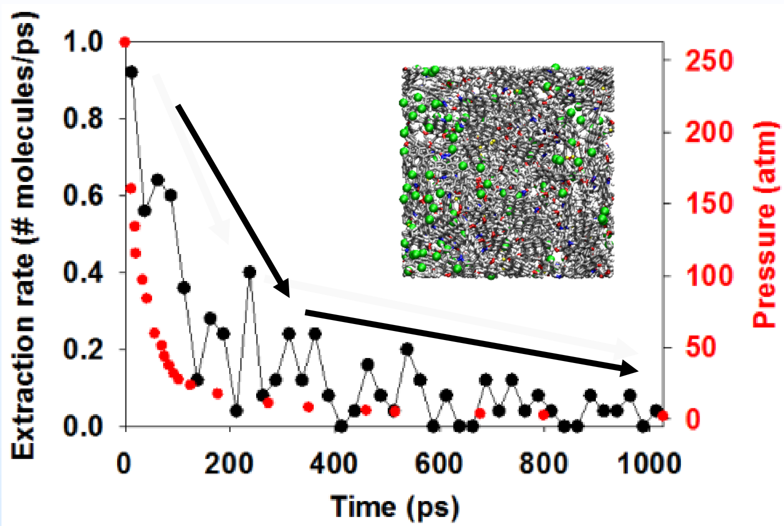


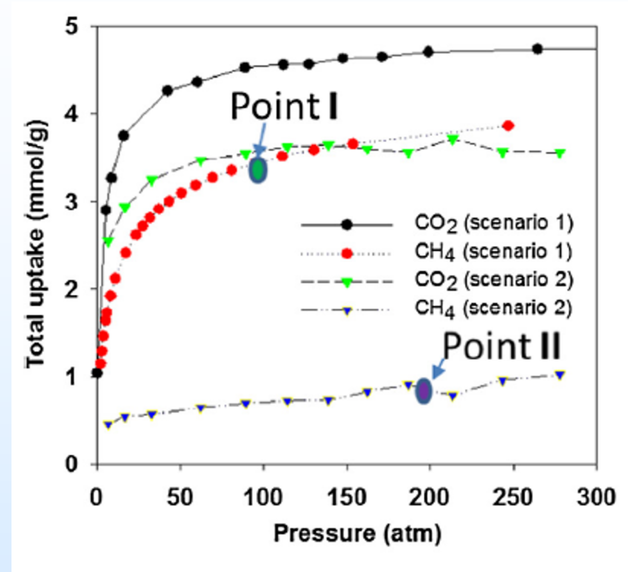
Accomplishments to Date

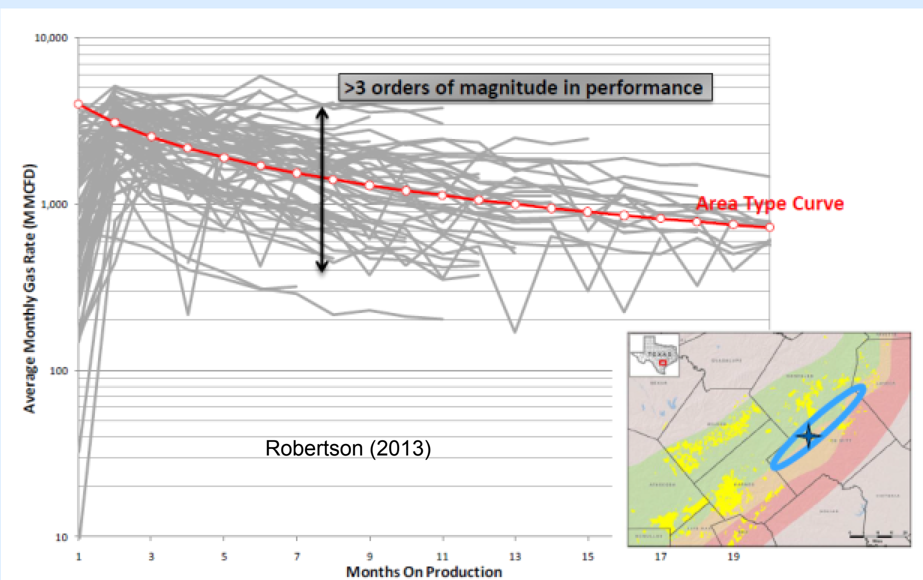
- Shale sample collection
- Gas sorption on clays and its implication to gas in place **(Xu et al., 2015)**
- Full cycle gas sorption/desorption on kerogen
- Interfacial chemistry and metal sorption/desorption on kerogen
- FTIR, NMR, DFT and MD studies of functional groups and structures of kerogens with different maturities **(Weck et al., 2017)**
- MD simulations of CH_4 sorption/desorption and release within kerogen **(Ho et al., 2016; Cristancho et al., 2016)**
- Competitive sorption of CO_2 over CH_4 on kerogen **(Ho et al., 2017)**
- MD simulations of the enhancement of water flow in a nanochannel by $scCO_2$ **(Ho et al., 2018)**
- MD and experimental study of chemical-mechanical coupling of gas adsorption onto kerogen **(Ho et al., 2018)**
- Experiments on kerogen reaction with supercritical CO_2 ($scCO_2$)
- MD simulations of selective gas permeation through shale matrix nanopores **(Ho and Wang, 2020)**
- Enhancement of oil flow in shale nanopores by manipulating friction and viscosity **(Ho and Wang, 2019)**
- Fundamental study of fast advective water flow in clay interlayers **(Ho et al., 2020)**
- Chemical and isotopic data collection and analyses of produced water from unconventional reservoirs **(Sharma et al., 2021)**
- Wettability alteration of subsurface porous media upon gas pressure variations **(Ho and Wang, 2021)**
- Nonlinear dynamics of fluid flow in low-permeability media: porosity waves and new mechanism

Technical Status

Q1: What controls the production decline rate?



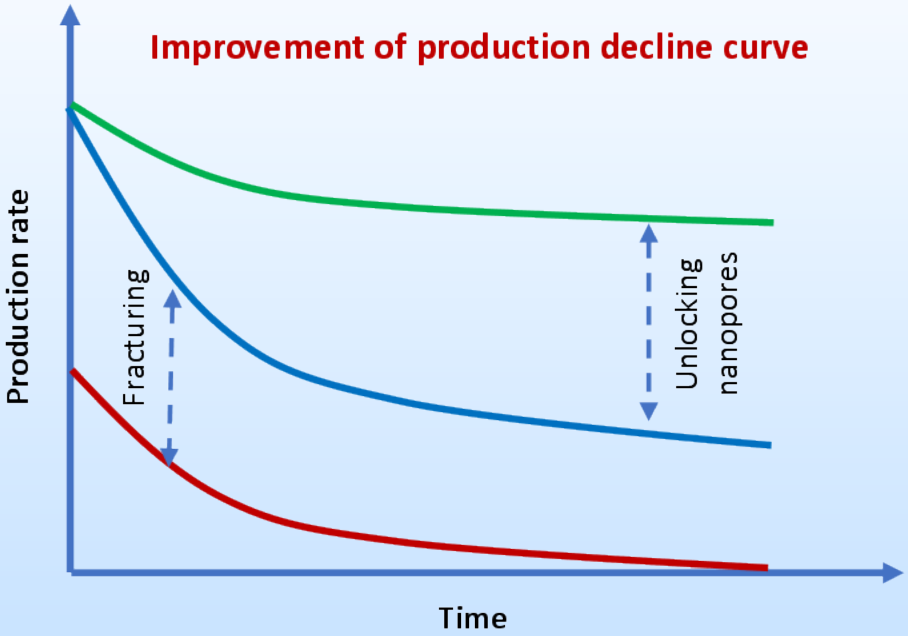




Q1: What controls the production decline rate?

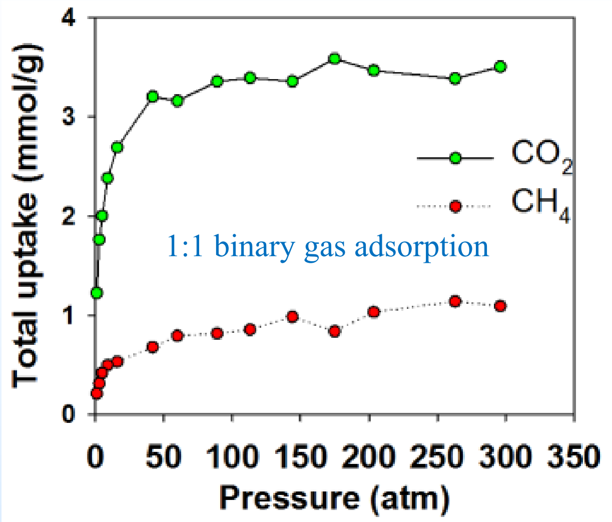
Answer:

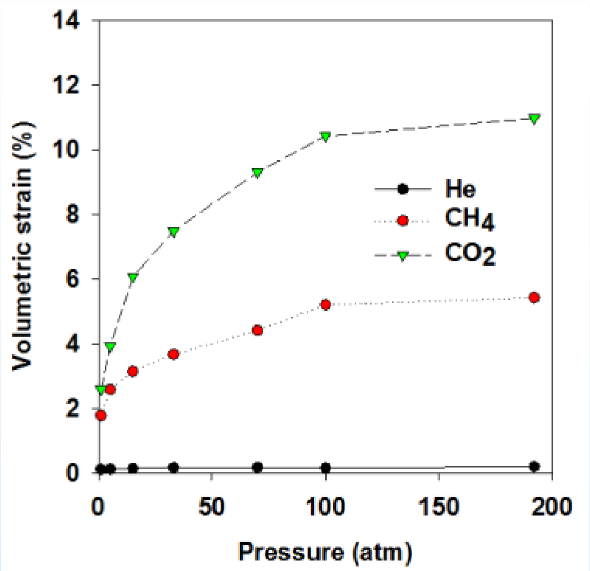
- The decline rate is an intrinsic property of a shale formation.
- A sensible way to improve the decline rate is to unlock shale nanopores.

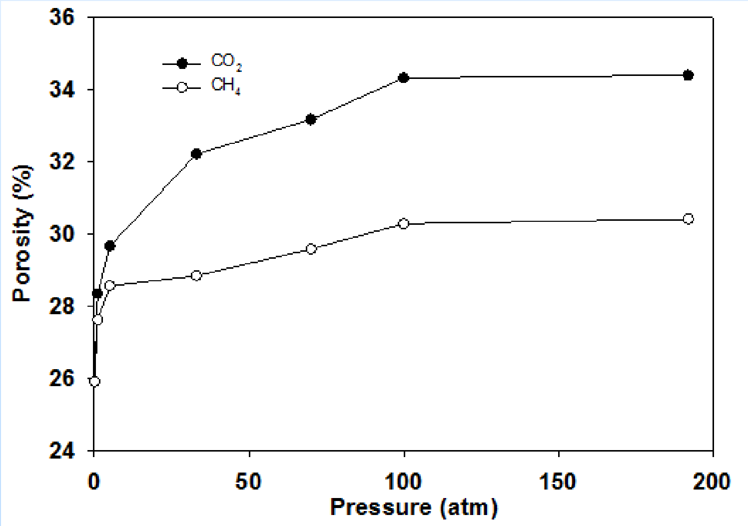


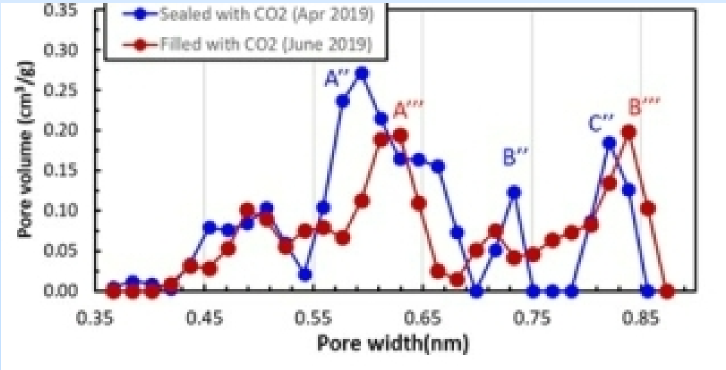
Technical Status

Q2: How to unlock shale nanopores?









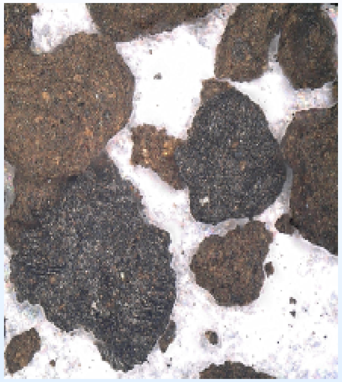
Swelling is controlled by the surface layer of gas adsorbed.

Experiments: Expose kerogen to 1 atm CO_2 and then measure pore size changes.

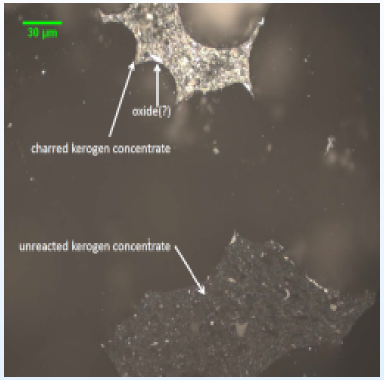
Kerogen reaction with supercritical CO_2

Original kerogen

Reacted kerogen



Reacted kerogen



Experiment: Immature kerogen reacted with supercritical CO_2 saturated brine (1M) at 90 °C and 2800 psi for 30 days

	Carbon	**Hydrogen**	**Nitrogen**	**Oxygen**	**Sulfur**	**Ash**	**C/H**	**C/O**	**C/N**
	% w/w	% w/w	% w/w	% w/w	% w/w	% w/w	atom	atom	atom
original kerogen	73.91	7.59	2.67	8.40	2.73	3.0	0.81	0.73	32.3
reacted residual kerogen	62.68	4.54	1.64	12.36	1.49	24.10	1.15	0.42	44.6

	S1	S2	S3	Tmax	Pyrolysable organic carbon	Residual organic carbon	TOC	Hydrogen index	Oxygen index	Mineral inorganic carbon
	mg HC/g	mg HC/g	mg CO_2/g	°C	% wt	% wt	% wt	mg HC/g TOC	mg CO_2/g TOC	% wt
original kerogen	5.63	412.11	6.47	431	35.24	37.97	73.21	563	9	0.93
reacted residual kerogen	1.91	181.38	13.54	424	16.23	33.90	50.13	362	27	11.89

Q2: How to unlock shale nanopores?

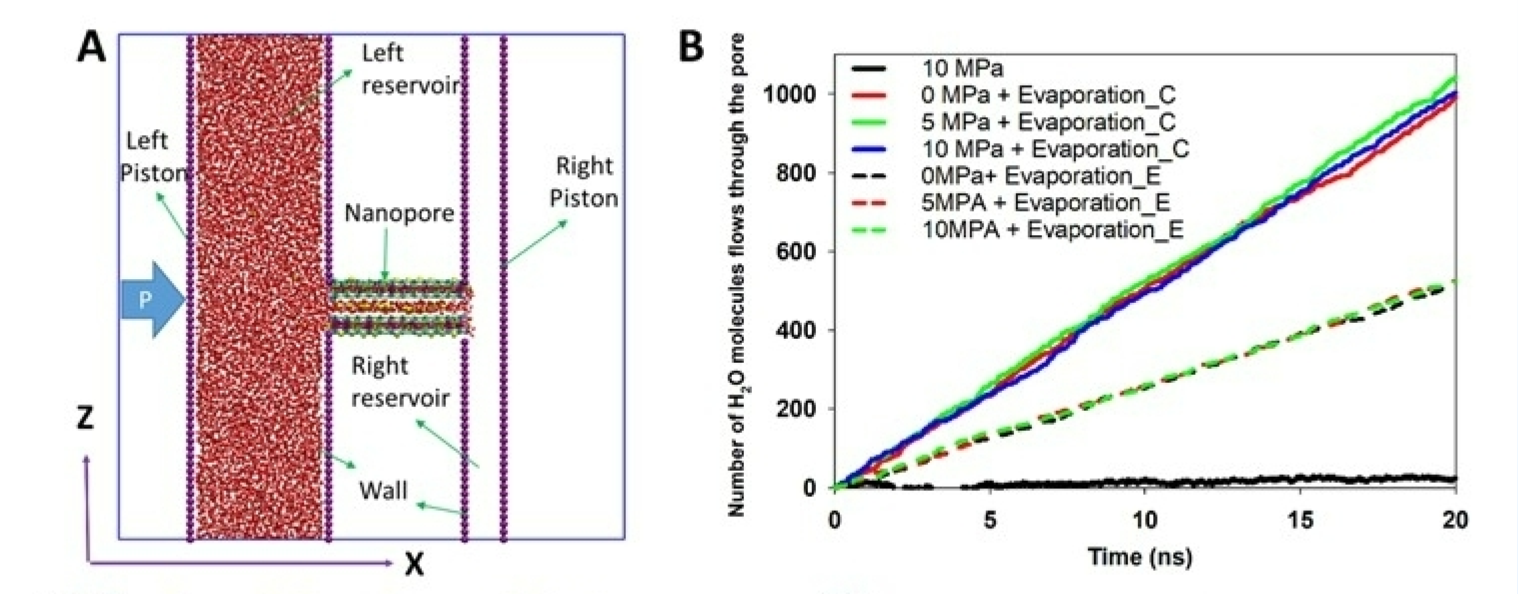
Answer:

- Shale nanopores can be unlocked by chemical displacement and chemical-mechanical coupling.
- Supercritical CO_2 is a stimulating agent for simultaneous gas extraction and carbon sequestration.

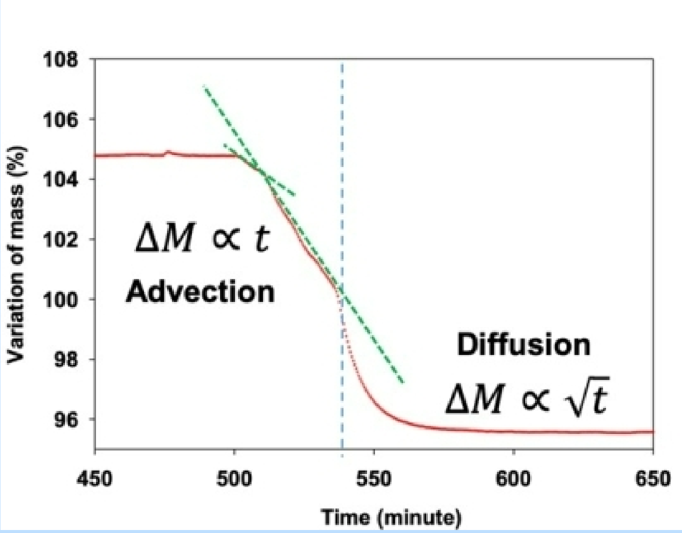
Technical Status

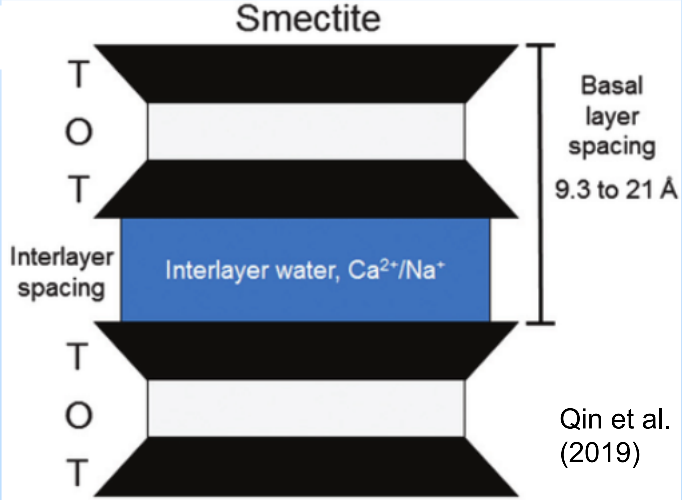
Q3: Can a fast advective flow occur in shale matrix?

MD simulations



Experiments



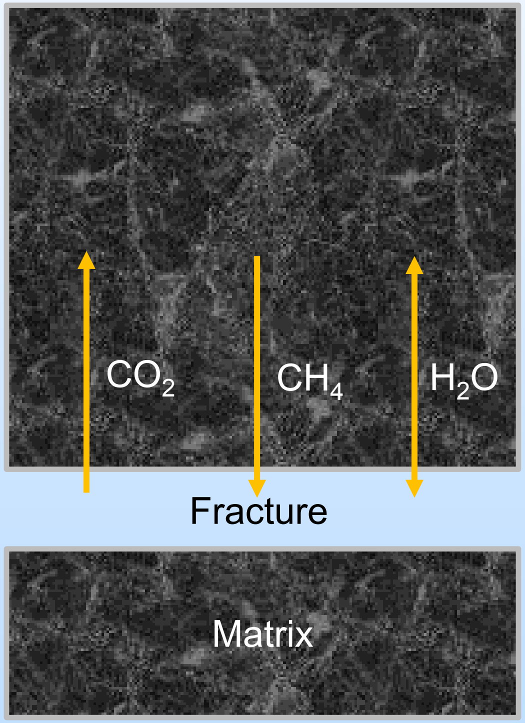


Qin et al. (2019)

Q2: Can a fast advective flow occur in shale matrix?

Answer:

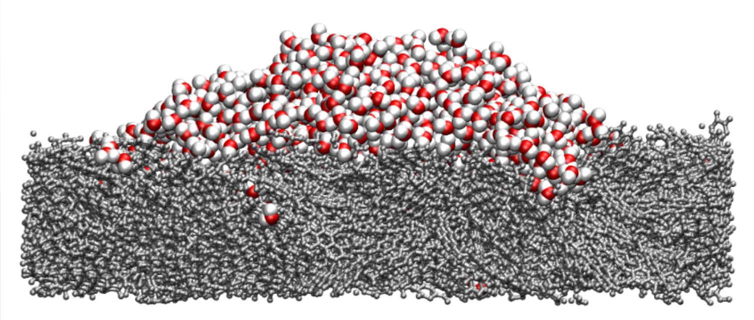
- Yes, it can be induced by a chemical gradient.
- Such flows have important implications to:
  - Water imbibition & loss during stimulation
  - Wellbore stability
  - Enhanced oil/gas recovery
  - Carbon sequestration



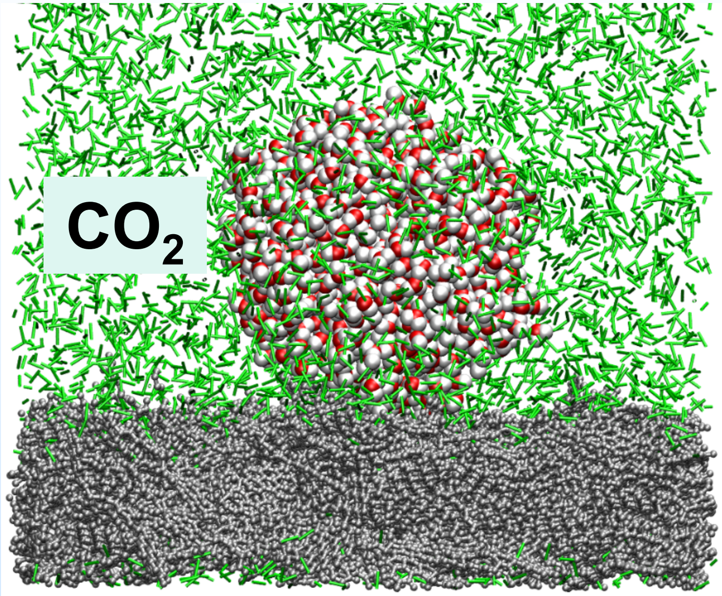
Technical Status

Q4: How much do we know about multicomponent and multiphase flows in shale matrix?

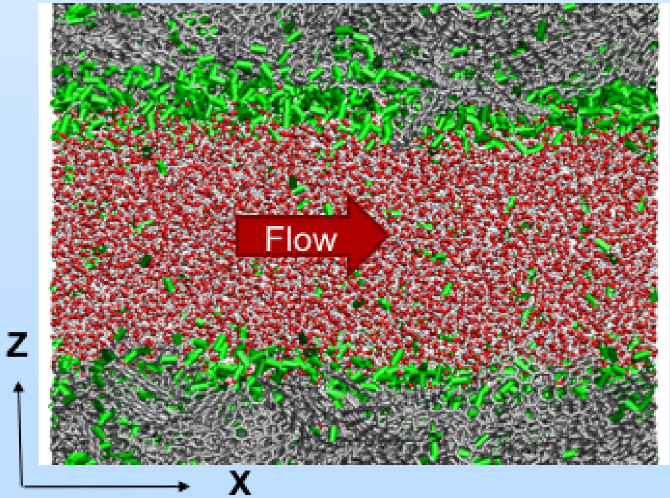
42.8°±6.5°



Low pressure

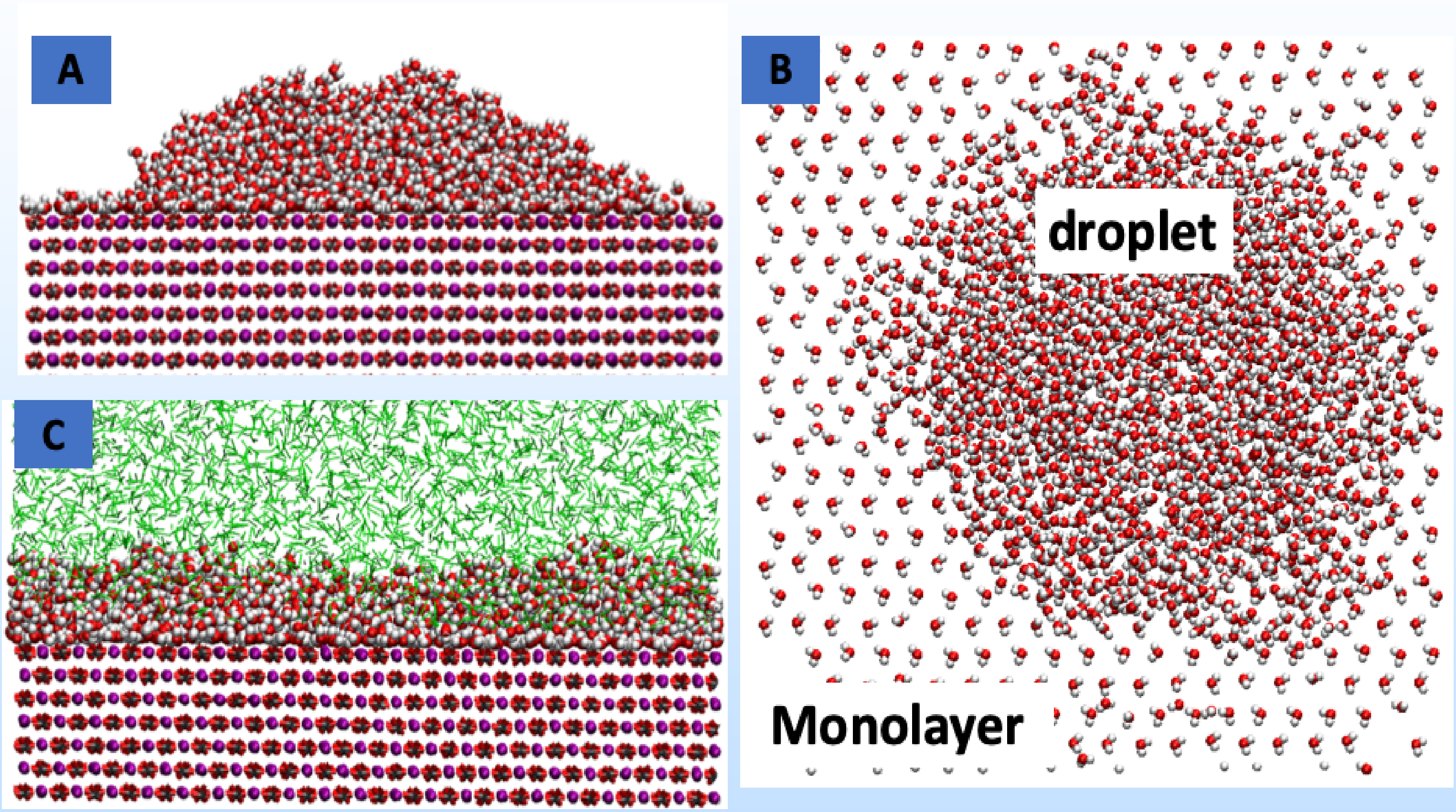


High pressure



CO_2 thin layer → Lubricant
Water flow rate enhanced by 4 times.

Surface wettability alteration with gas pressure



Water drop on calcite

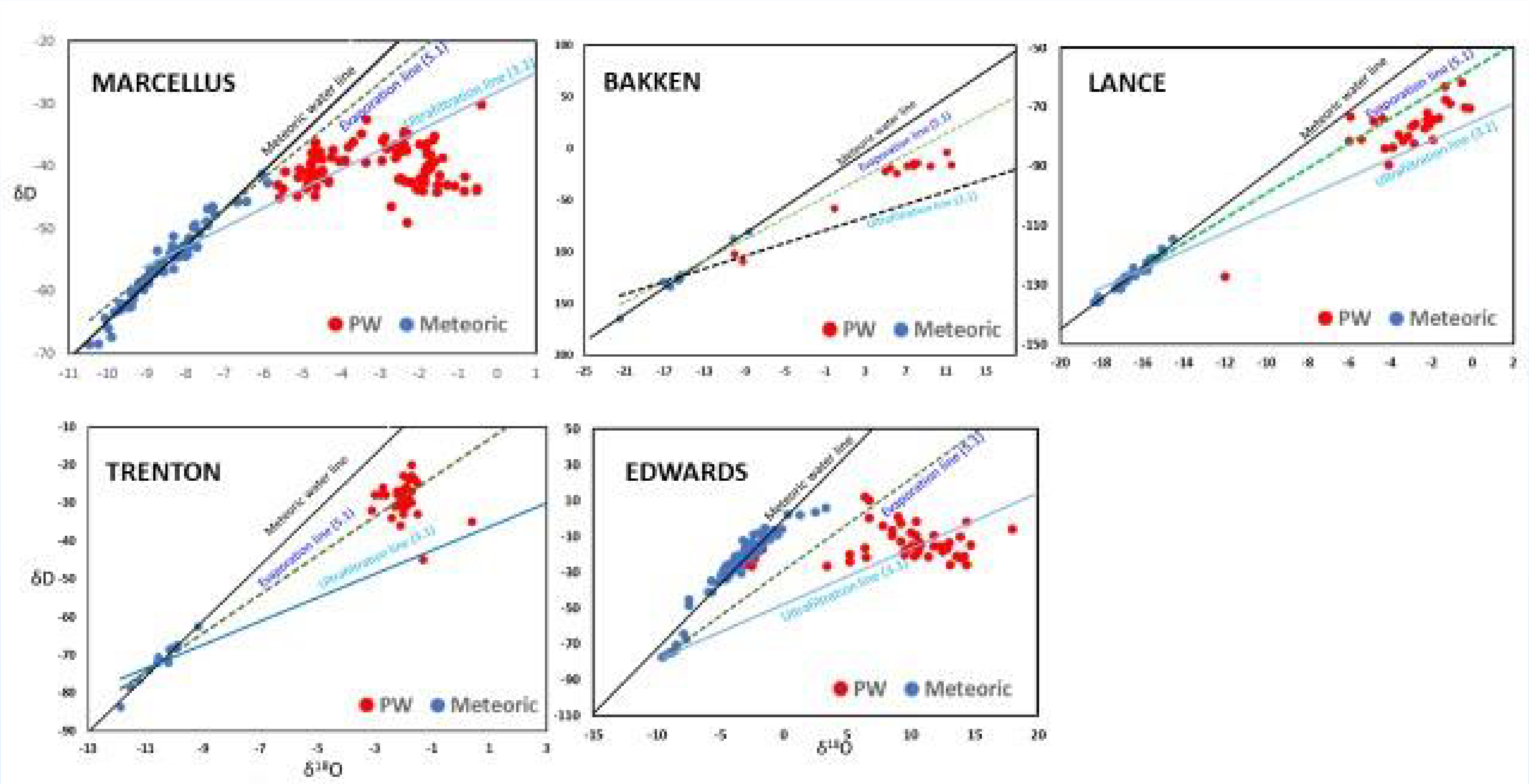
Q4: How much do we know about multicomponent and multiphase flows in shale matrix?

Answer:

- Much remains to be learned.
- Challenge: complex phase transition + complex nanopore networks

Technical Status

Q5: How to bridge nanoscale understandings to field observations?



Nonlinear dynamics of fluid flow in deformable low permeability media: Porosity waves

$$\frac{\partial \phi}{\partial t} = \nabla \cdot (k f \phi^2 \nabla P)$$

Continuity for fluid

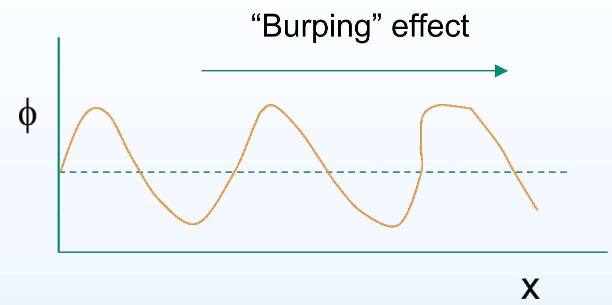
$$\frac{\partial \phi}{\partial t} = \lambda[\frac{R_d E}{2G_d^2}\tau^2 + P - I - (\phi - \phi_0)E]$$

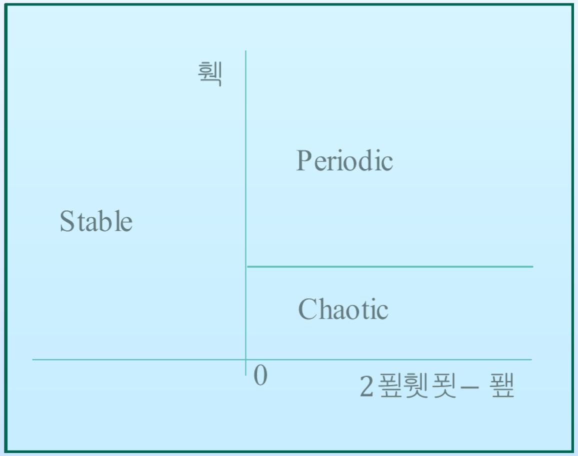
Shear induced dilatancy

$$f = \frac{\alpha \tau^n \phi^m}{1 + \alpha \tau^n \phi^m}$$

$$\tau = \frac{G_d \sqrt{J}}{G_d - (f + \beta \nabla^2 f)(G_d - G_w)}$$

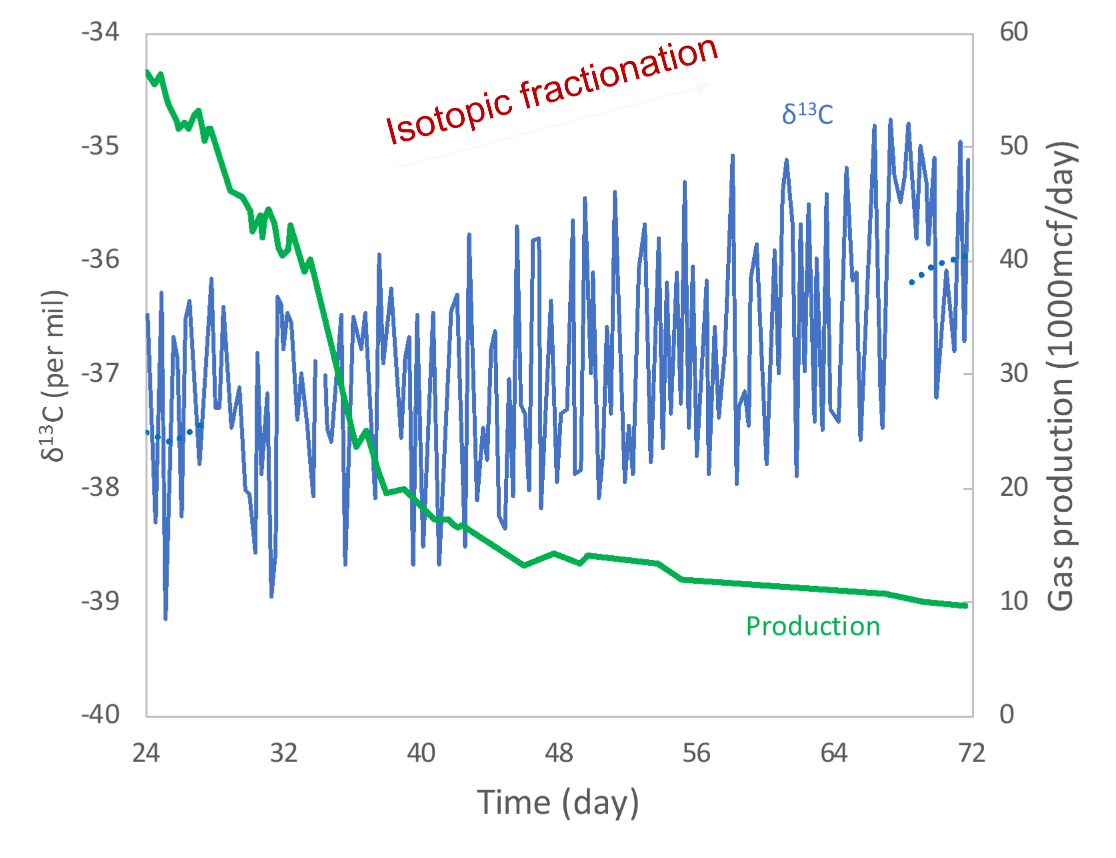
Stress partitioning/fluid-induced weakening





Wang et al. (2020)

Porosity waves & episodic gas release in shale gas production



Implications:

- New mechanism for shale/oil release from shale matrix?
- New method for stimulation?
    - Create porosity waves
    - Especially for ductile shale
- Synchronized huff-puff

Yongchun Tang,
PEERI

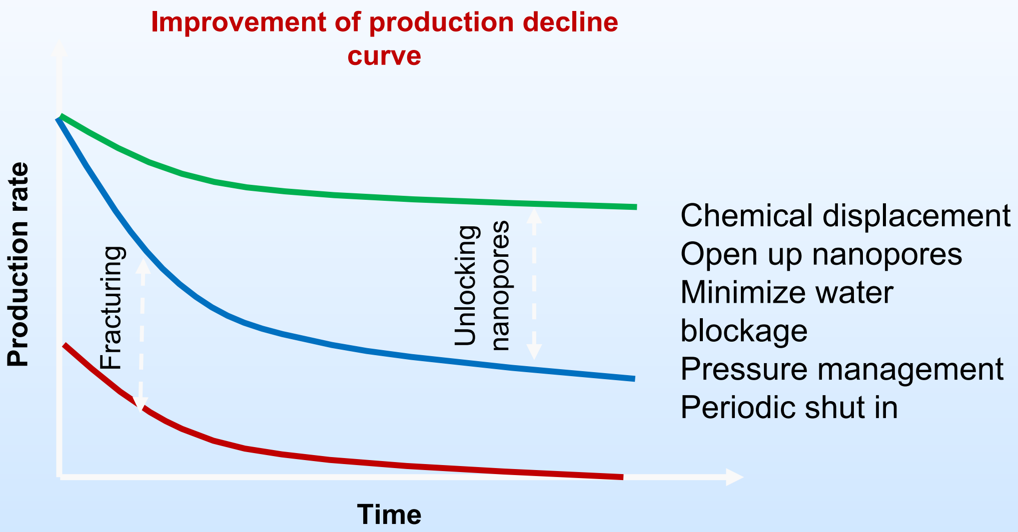
Q5: How to bridge nanoscale understandings to field observations?

Answer:

- Nanoscale understanding provides a scientific basis for field-scale observations.
- It also helps understand emerging transport processes and develop a new stimulation strategy (porosity waves).

Project Summary

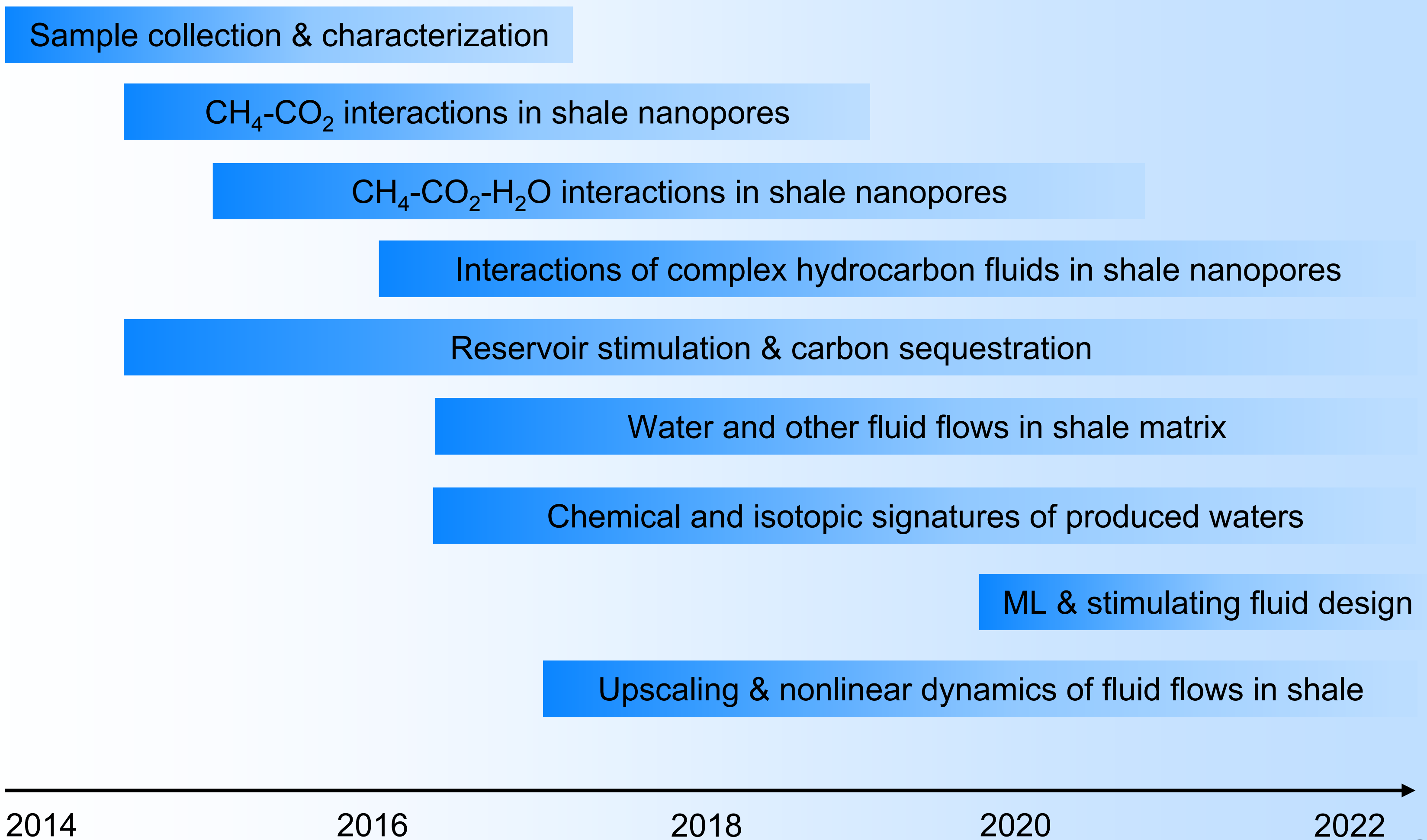
- Nanopore confinement plays a critical role in gas disposition and release in unconventional reservoirs.
- Our work reveals complex interactions of CH_4-CO_2-H_2O in shale nanopores.
- Mechanistic understanding of these interactions will help explore possible ways to unlock shale nanopores.
- Such understanding is critical to design an effective stimulation, EOR and carbon management strategy for shale oil/gas extraction.



Benefit to the Program

- Fewer wells with less environmental impact for shale gas production
- Carbon management in unconventional reservoirs
    - Reducing carbon footprint by simultaneous carbon sequestration for gas production
    - Large capacity; much less relying on structural trapment (e.g. caprocks in conventional reservoirs)
    - Reutilization of existing infrastructures; distributed operations

Activities & Schedule



Lessons Learned

NATIONAL ENERGY TECHNOLOGY LABORATORY

Los Alamos NATIONAL LABORATORY

SLAC NATIONAL ACCELERATOR LABORATORY

BERKELEY LAB Lawrence Berkeley National Laboratory

Sandia National Laboratories

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