New Imaging and CO_2 Storage Technologies for Unconventional Subsurface Reservoirs

Task 1: Enhanced Contrast Agents for CO_2 Monitoring

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National Energy Technology Laboratory

Addressing the Nation's Energy Needs Through Technology Innovation – 2019 Carbon Capture, Utilization, Storage, and Oil and Gas Technologies Integrated Review Meeting

Presentation Outline

- Program Focus Area and DOE Connections
- Goals and Objectives
- Scope of Work
- Technical Discussion
- Accomplishments to Date
- Appendix (Organization Chart, Gantt Chart, and Bibliography

Benefit to the Program

- Program goals addressed:
  - Technology development to predict CO_2 storage capacity
  - Demonstrate fate of injected CO_2
- This research addresses the following Priority Research Directions recommended in the Mission Innovation CCUS Workshop report:

S-1: Advancing Multiphysics and Multiscale Fluid Flow to Achieve Gt/year Capacity

S-4: Developing Smart Convergence Monitoring to Demonstrate Containment and Enable Storage Site Closure

Project Overview:
Goals and Objectives

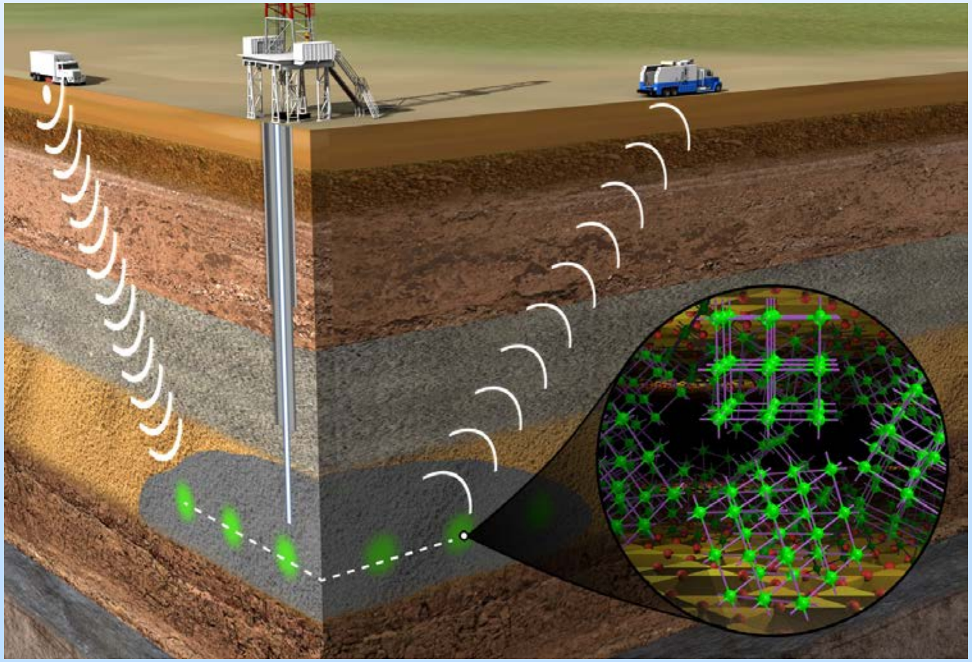
- Goal: Development of geologic storage technology with a near zero cost penalty goal – a grand challenge with enormous economic benefits.
- Objective: Employ a multidisciplinary approach for identifying key sequestration opportunities and for pursuing major research needs in for development of acoustically responsive contrast agents for enhanced monitoring of injected CO_2.

Enhanced Contrast Agents for CO_2 Monitoring

Problem Statement: Current monitoring techniques for detecting and surveying injected fluids and fracture networks suffer from low detection sensitivity and limited volumetric resolution

- Engineering nanomaterials for subsurface injection
- Dispersion in $scCO_2$ (and other fluids) to form nanofluids
- Detection through conventional seismic imaging

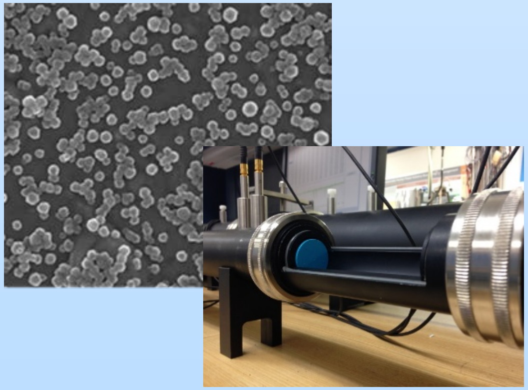
Goal: Develop contrast agents for time-resolved monitoring/mapping of subsurface fluids and fracture networks

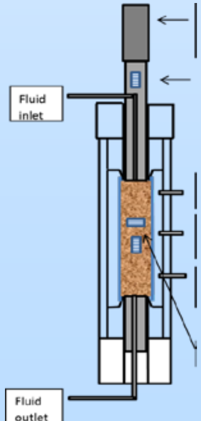


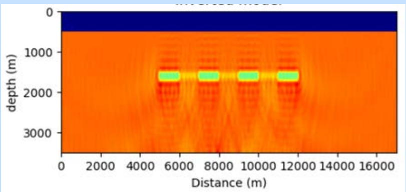
Project Overview

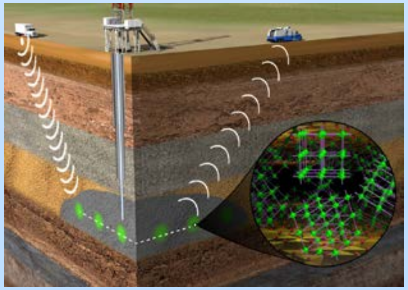
- Task 1 – Enhanced Monitoring Agents
  - 1.1 Synthesis of acoustically-responsive contrast agents
  - 1.2 Laboratory-based core test experiments
  - 1.3 Numerical modelling of seismic wave propagation and reflections
  - 1.4 Field test plan development

Synthesis ⟷ Experiments ⟷ Simulations ⟷ Field Test Plan



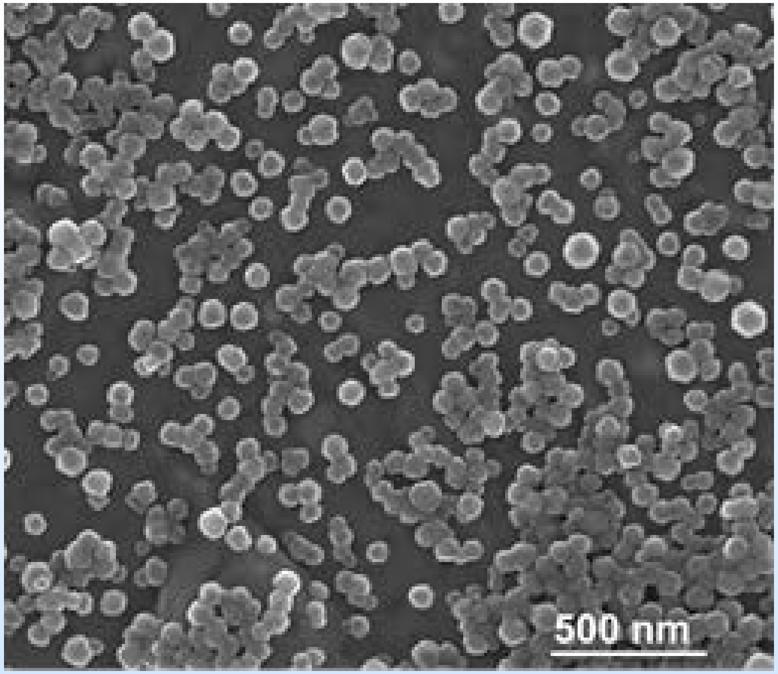






Metal-Organic Framework Nanoparticles

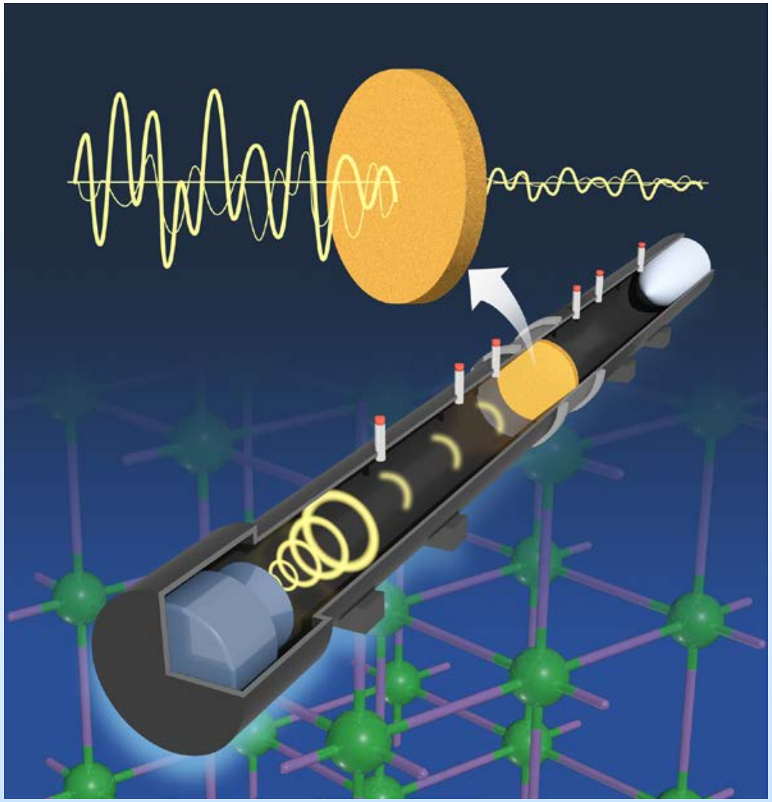
- Injectable nanoparticles
- Ultra-high surface area
- Defect engineering and flexibility modifications
- Metal-organic frameworks have anomalous low-frequency sound attenuation properties
- Laboratory geophysical experiments indicate MOF nanofluids alter the elastic and anelastic properties of fluid-bearing rocks
- These microporous materials may be used as acoustic contrast agents for better resolving subsurface fluids and structures



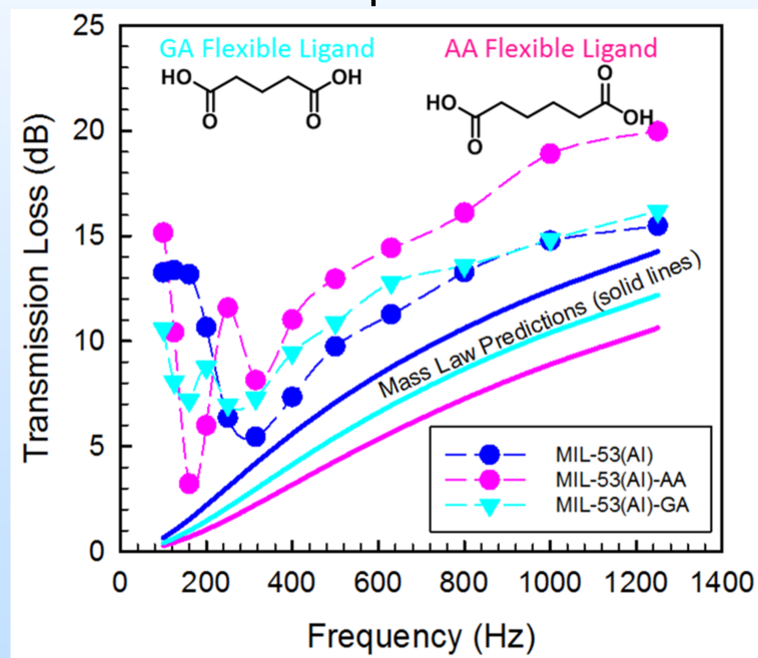
Applications/Significance/Novelty

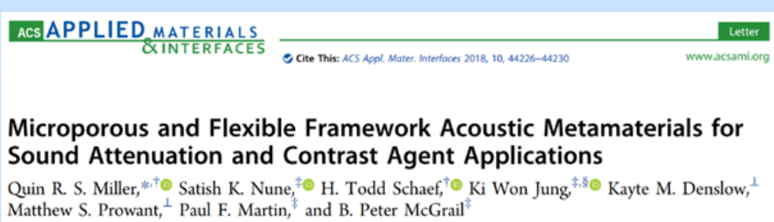
Our MOF nanofluid approach enhances conventional seismic monitoring by substantially altering the velocity and amplitude of low-frequency waves

MOFs are Acoustic Metamaterials



- Deviation from mass law by MOFs indicate unusual absorptive acoustic properties relative to natural rock materials
- Substitution of flexible ligands glutarate and adipate forms flexible framework MIL-53(Al) and new resonance peaks





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Microporous and Flexible Framework Acoustic Metamaterials for Sound Attenuation and Contrast Agent Applications

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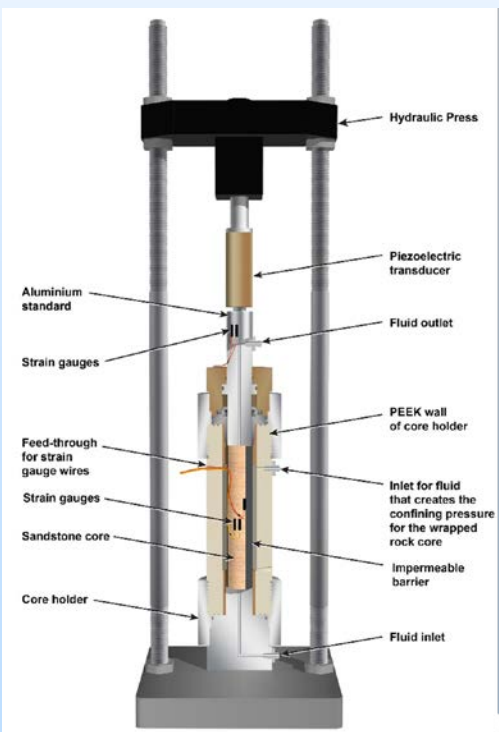
Engineered flexibility of the framework structure may be undertaken to increase attenuation and tune characteristics for each application

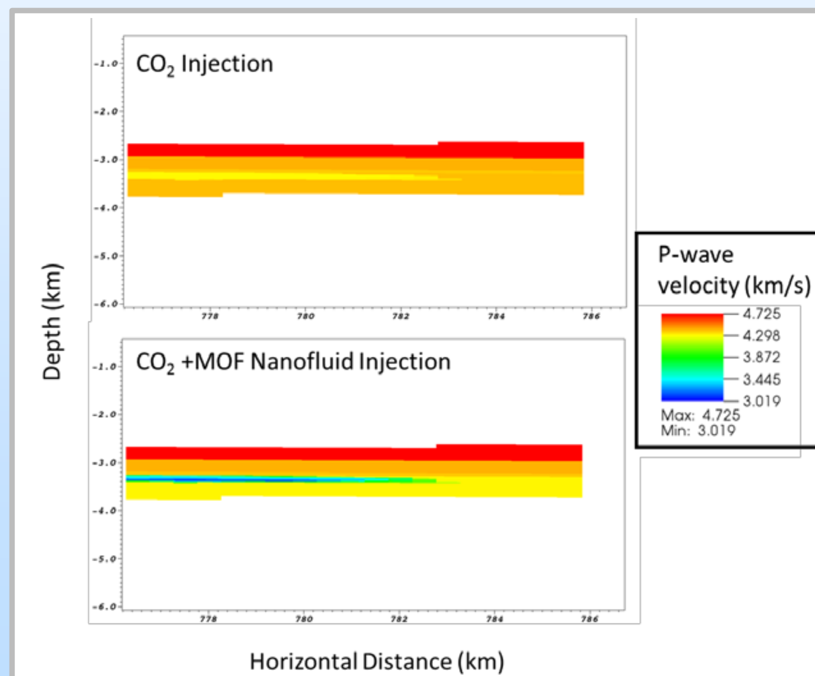
MOFs Influence Elastic and Anelastic Rock Properties

Forced oscillation laboratory technique utilized to measure elastic and anelastic properties of sandstone cores at relevant frequencies (1-100 Hz)

- Reduction in Young's modulus and increase in attenuation due to injection of 0.5 wt% MOF nanofluids (Schaef et al. 2017 and Miller et al. 2019)

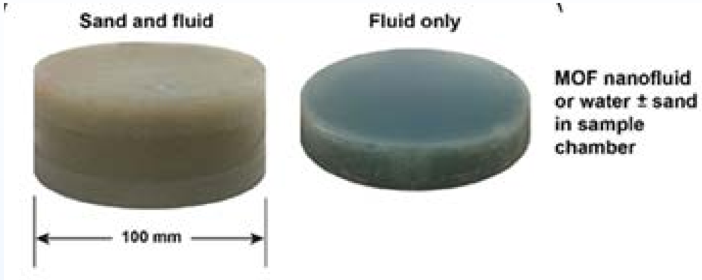


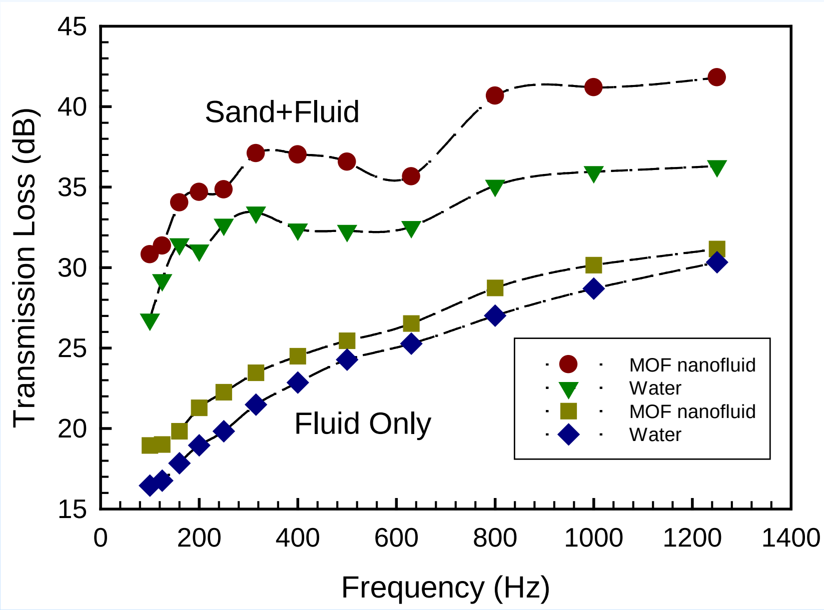
0.2% increase in mass per 5 PV



~30% decrease in P-wave velocity

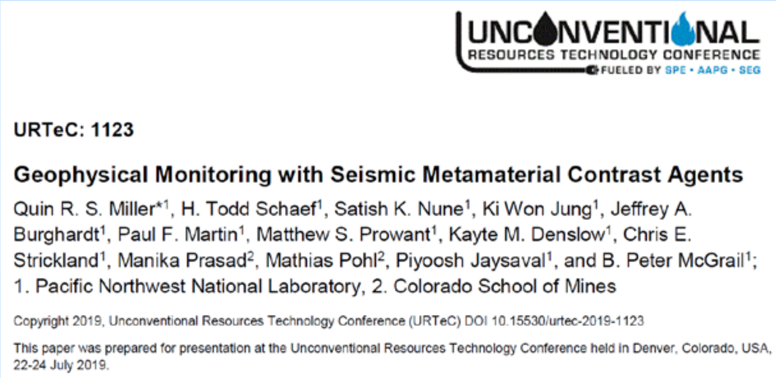
Mechanistic Insights





Transmission loss experiments confirm that contrast agent nanofluids possess intrinsic properties that contribute to low-frequency attenuation, although the magnitude is small

- Changes to Young's Modulus likely due to rock-nanofluid interfacial effects
- A portion of the observed attenuation due to MOF in the bulk pore fluid
- 10X increase in surface area of the rock-fluid-MOF system greatly increases internal reflections, resonances, and scattering of low-frequency waves with only a 0.5 wt% nanofluid concentration
- Wettability alteration or surface charge effects?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URTeC: 1123

Geophysical Monitoring with Seismic Metamaterial Contrast Agents

Quin R. S. Miller*[1], H. Todd Schaef[1], Satish K. Nune[1], Ki Won Jung[1], Jeffrey A. Burghardt[1], Paul F. Martin[1], Matthew S. Prowant[1], Kayte M. Denslow[1], Chris E. Strickland[1], Manika Prasad[2], Mathias Pohl[2], Piyoosh Jaysaval[1], and B. Peter McGrail[1];
1. Pacific Northwest National Laboratory, 2. Colorado School of Mines

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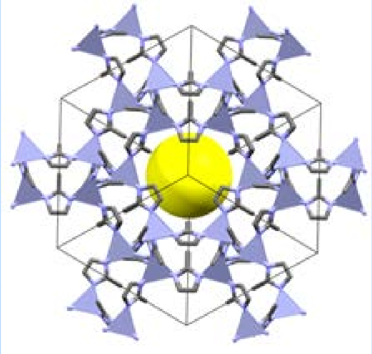
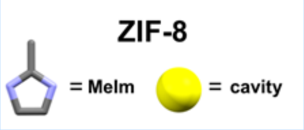
MOF Nanoparticle Synthesis

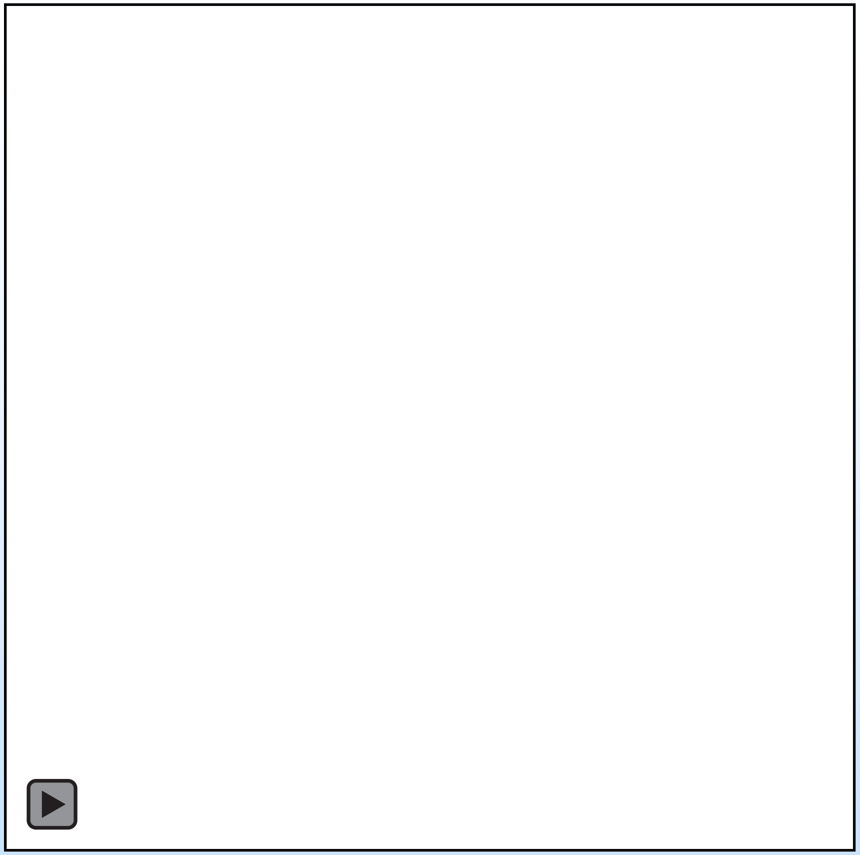
Goals: Rapid production of resilient Zr, Zn, and Fe-based MOF frameworks with high-colloidal stability, some with core@shell structures

Four new nanofluids:

- UiO-66
- Polymer-coated MIL-100(Fe)
- ZIF-8 (three different synthesis procedures)



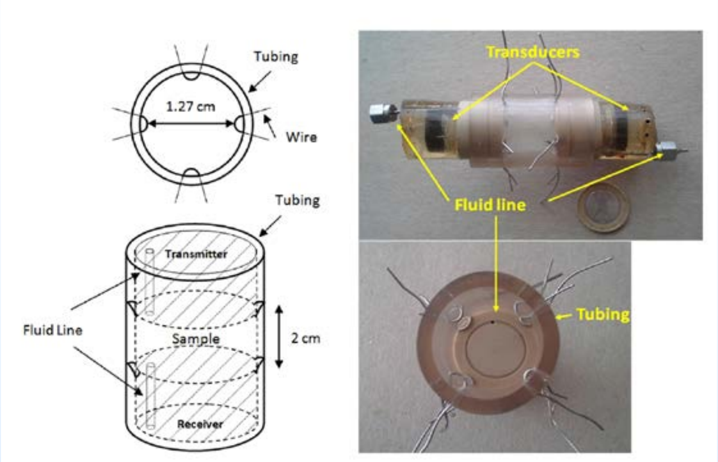




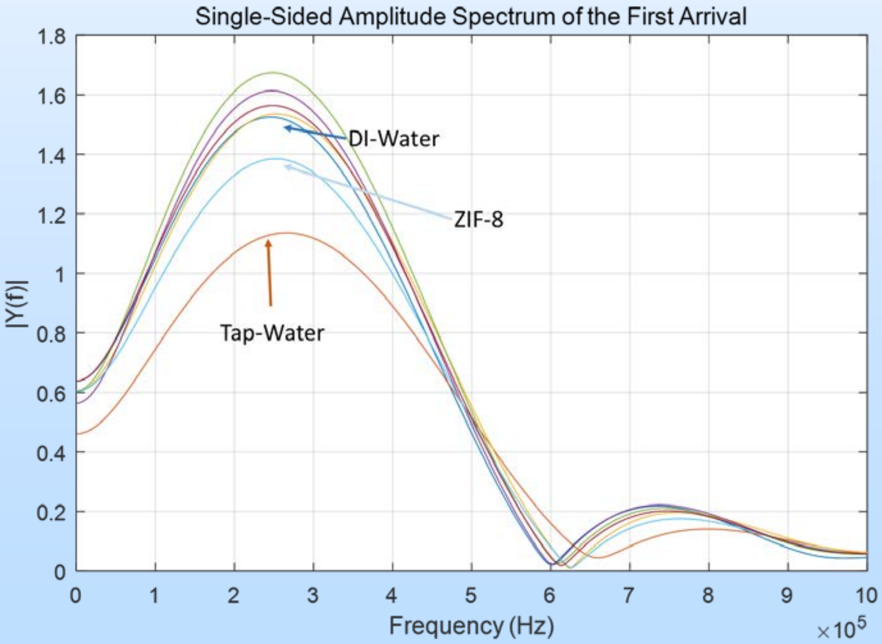
Transformation of nanoZnO to nanoZIF-8 in supercritical CO_2 monitored by high pressure in situ XRD at 60 °C and 90 bar

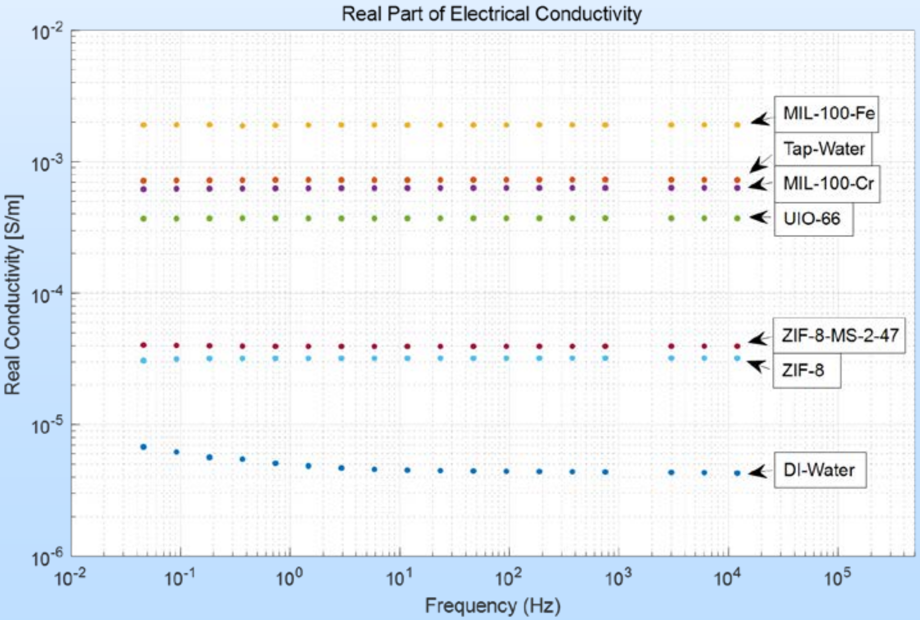
Ultrasonic and Electrical Properties of MOF Contrast Agent Nanofluids

- Evaluated the ultrasonic velocity and attenuation of five MOF nanofluids
- Probed electrical properties of nanofluids, potential for multi-use contrast agents



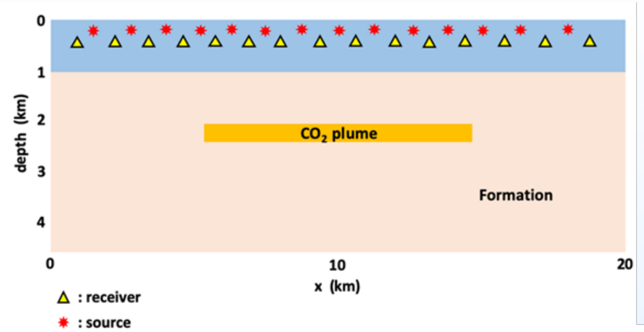
Ultrasonic fluid cell (Pohl, Prasad, Batzle 2018)

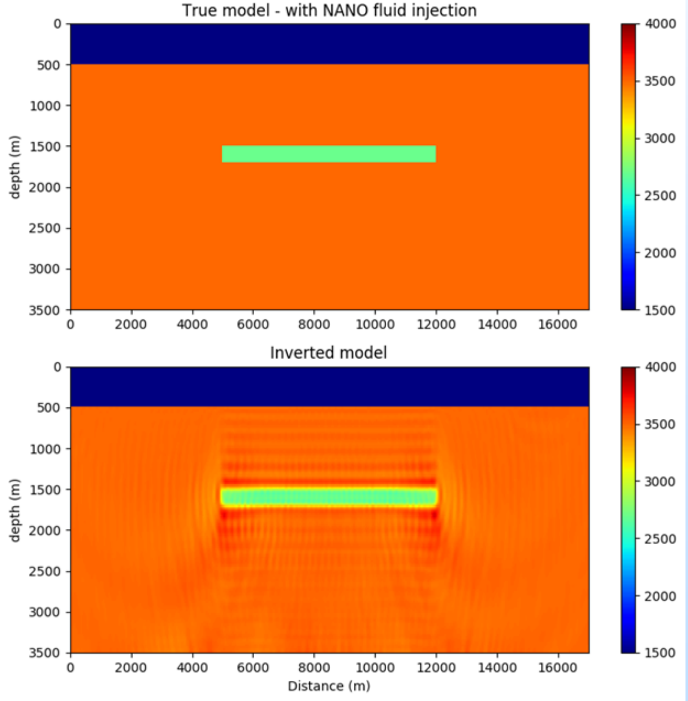


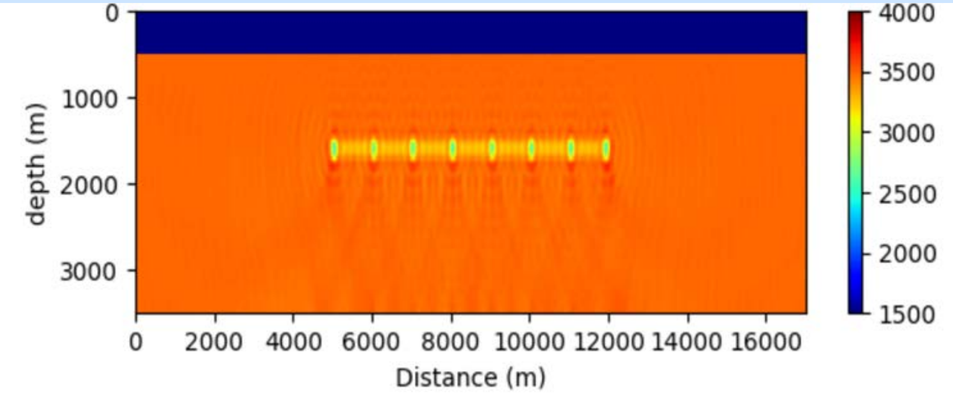


Full-Waveform Inversion Seismic Simulations

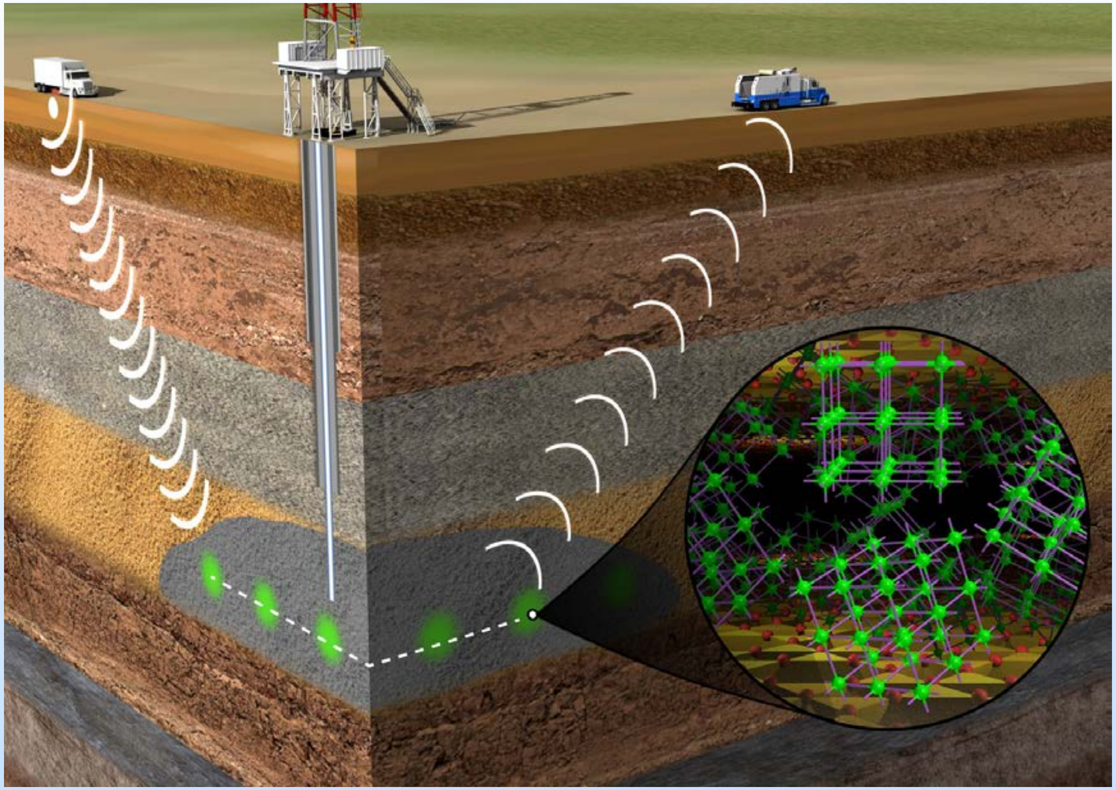
- What are the effects of injectates (MOF nanofluids) on wave propagation behaviors (e.g., refraction, reflection, dissipation and attenuation)?
- SEISCOPE simulations used to model seismic wave interactions with H_2O-, CO_2-, and nanofluid-saturated reservoir rocks. This model can incorporate velocity information for the overlaying formations, reservoir, and CO_2 plume.
- Continuing FWI simulations to create stepwise complexity in the 2D placement of MOF nanofluids, four injectate spacings (125-1000 m) tested







Multiscale Metamaterials in the Subsurface



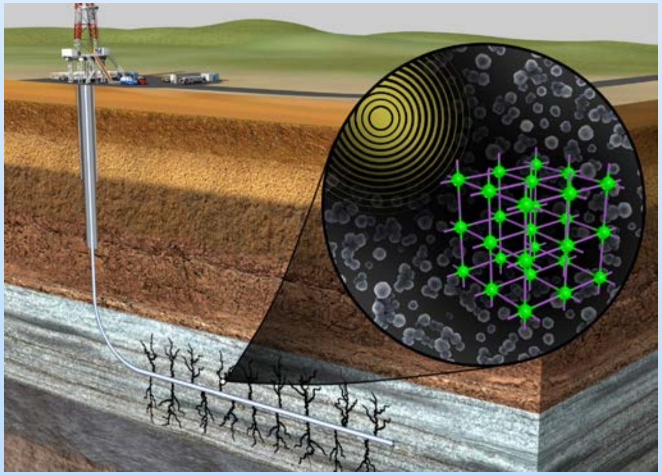
- nm- to km-scale 3D arrays
- Injectable metamaterials key to imposing reservoir-scale periodic structure for seismic wave manipulation
- Emergent properties of metamaterial arrays could include:
  - Resonant periodic structures in the subsurface
  - Acoustic lensing, focusing and amplification
  - Increase in resolution for better delineating spatial relationships of fluids and pore/fracture networks

Critical Parameters for Field Test Plan

- **0.1 wt% MOF nanofluid concentrations**
- **Polymer coatings to ensure colloidal stability**
- **Episodic injection to minimize injected material**
- **Nanofluid alternating gas "NAG" injection to impose periodic subsurface structures**

Ongoing and Future Work

- FY20 focused on optimizing each parameter for a field site of interest, with contrast agent properties (MOF composition/topology and surface coatings) and injection strategies tailored to lithology, formation fluid chemistry, and reservoir structure.
- Identify a field test injection site and industry partner, continue to fine tune field test plan.
- Determine the exact mechanism(s) of seismic wave-MOF interactions via continued experimentation and related forward modelling.
- O&G and GTO synergies



Accomplishments to Date

- First to examine the acoustic properties of MOFs, demonstrated that they are acoustic metamaterials
- Continued developments of nanofluid synthesis procedures, include MOF@polymer and ZnO@ZIF-8 core-shell composites
- Parameterized velocity and FWI seismic models with low-frequency core test results
- Initiated successful ongoing collaboration with Prof. Manika Prasad's research group at CSM
- Demonstrated MOF nanofluids have distinctive electrical signatures
- Work published in ACS Applied Materials and Interfaces and URTeC conference proceedings
- Results presented at AGU, URTeC, and ACS

Acknowledgements

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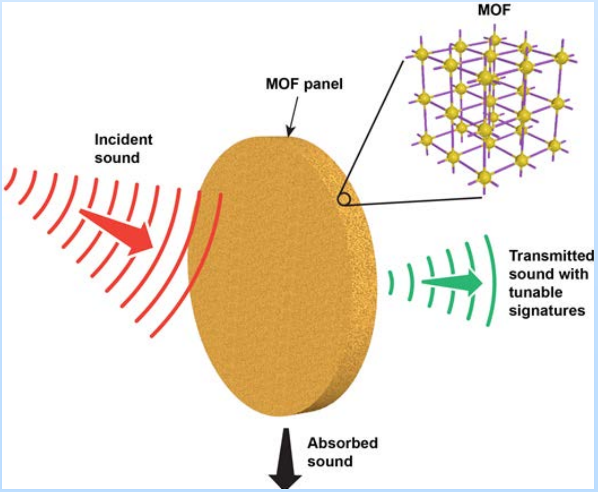
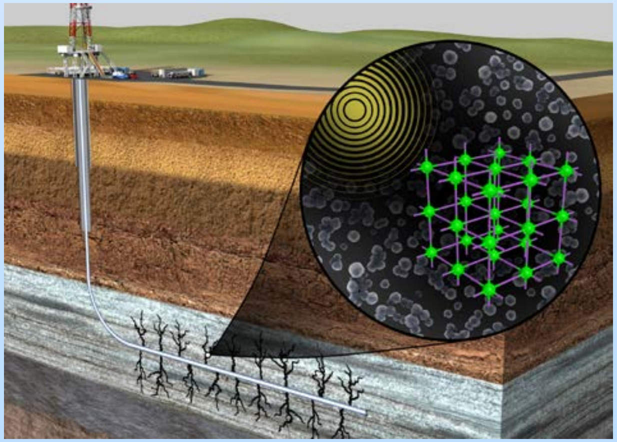
Manika Prasad, Mathias Pohl, Jyoti Behura

Jeff Burghardt, Piyoosh Jaysaval, Michael Sinnwell, Paul Martin, Matt Prowant, Kayte Denslow, Ki Won Jung, Chris Strickland

Relevant Publications

- 1. Miller, Q.R.S., H.T. Schaef, S.K. Nune, K.W. Jung, J.A. Burghardt, P.F. Martin, M.S. Prowant, K.M. Denslow, C.E. Strickland, M. Prasad, M. Pohl, P. Jaysaval, B.P. McGrail. **(2019)** “Geophysical Monitoring with Seismic Metamaterial Contrast Agents”. Unconventional Resources Technology Conference (URTeC) Proceedings., DOI:10.105530/urtec-2019-1123.
- Miller, Q.R.S, Schaef, H.T., Nune, S.K., Jung, K.W., Denslow, K.M., Prowant, M.S., Martin, P.F., McGrail, B.P. (**2018)**. “Microporous and Flexible Framework Acoustic Metamaterials for Sound Attenuation and Contrast Agent Applications”, ACS Applied Materials & Interfaces, 10, 51, 44226-44230
- Schaef, H.T., Strickland, C.E, Jung, K.W., Martin, P.F., Nune, S.K., Loring, J.S., McGrail, B.P. (**2017**) “Injectable Contrast Agents for Enhanced Subsurface Mapping and Monitoring”, Energy Procedia 114, 3764-3770





Appendix

– These slides will not be discussed during the presentation, but are mandatory

Organization Chart

- Project team has participants that cut across the Energy & Environment and Fundamental Sciences Directorates at PNNL
- Pacific Northwest National Laboratory is Operated by Battelle Memorial Institute for the Department of Energy

Gantt Chart

Detailed Schedule

FY 2018: July | Aug | Sept | Oct | Nov | Dec | Jan | Feb | March | April | May | June

#	Task Name Project Management	Start	Finish
1	Manage Project	Jul-18	Jun-19
2	FY18 Q1 Report	Jul-18	Sep-18
3	FY18 Q2 Report	Oct-18	Dec-18
4	FY18 Q3 Report	Jan-19	Mar-19
5	FY18 Q4 Report	Apr-19	Jun-19

#	Milestone Description	Milestone Date
6	Continue core testing with the newly designed apparatus developed in FY17. The core testing objectives will be focused on down selecting those acoustic responsive materials developed in FY17 that would be the best candidates for field deployment.	Sep-18
7	Complete data collection on the dry CH4-CO2 fluid system with the cation variable smectite clays. The data will include those generated from the NMR, XRD, and IR techniques and will be submitted to subtask 2.2 for analysis. This activity will also include collaboration with our university partners.	Sep-18
8	Continue core testing with the newly designed apparatus developed in FY17. The core testing will be focused on down selecting those acoustic responsive materials developed in FY17 that would be the best candidates for field deployment. Outcomes from this activity will be transferred to subtask 2.2, simulations.	Dec-18
9	Finalize data analysis on methane sorption to dry Ca, Na, NH4, and Cs montmorillonite including those molecular simulations from our university partners and summarize into a manuscript for submission into a peer review journal.	Dec-18
10	Complete development of an acoustic-wave model to solve acoustic- and elastic-wave equations. This will involve using algorithms to simulate compressional- and shear-wave forward propagation and reflections from numerical models with the properties of the natural core material and those cores containing nanomaterials, and compare the simulated waveforms with measured ones.	Mar-19
11	Complete data collection on the wet CO2-CH4 mixture and Na, NH4 and Cs montmorillonites. The data will include those generated from XRD and IR techniques and will be submitted to subtask 2.2 for analysis. This activity will also include collaboration with our university partners.	Mar-19
12	Finalize field deployment plans for injecting acoustically responsive contrast nanomaterial based fluids into an active CO2 field demonstration site. Core tests and seismic modeling conducted under subtask 2.1 and 2.2 will provide key parameters such as expected seismic signal, fluid injection rates, and nanomaterial concentration in the injected fluid. Staff will report results from a series of field-scale simulations with STOMP-CO2.	Jun-19
13	Finalize data analysis on wet CO2-CH4 fluids that are exposed to Na, NH4 and Cs montmorillonites and summarize into a manuscript for submission into a peer review journal.	Jun-19

Project: New Imaging and Permeability Control Technologies for Subsurface Reservoirs

Task | Milestone ◆ | Phase | Quarterly Report | Milestone Completed ☆