Enhanced Contrast Agents for CO_2 Monitoring

Project Number 70066

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U.S. Department of Energy

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Mastering the Subsurface through Technology Innovation, Partnerships, and Collaboration: Carbon Storage and Oil and Natural Gas Technologies Review Meeting

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Presentation Outline

- Program Focus Area and DOE Connections
- Goals and Objectives
- Scope of Work
- Technical Discussion
- Accomplishments to Date
- Project Wrap-up
- 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
- Project benefits statement: This research project conducts modeling and laboratory studies to lower cost and to advance understanding of storing pure CO_2 and mixed gas emissions produced from post- and oxy-combustion flue gas in unconventional geologic reservoirs.

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:
  - Identifying R&D needs and pursuing R&D on promising low-cost technologies for utilizing CO_2 and CO_2 containing other constituents in depleted shale gas and shale oil reservoirs.
  - Fate and transport of supercritical gas mixtures in fractured geologic formations.
  - Development of acoustically responsive contrast agents for enhanced monitoring of injected CO_2.

Project Overview:
Scope of work

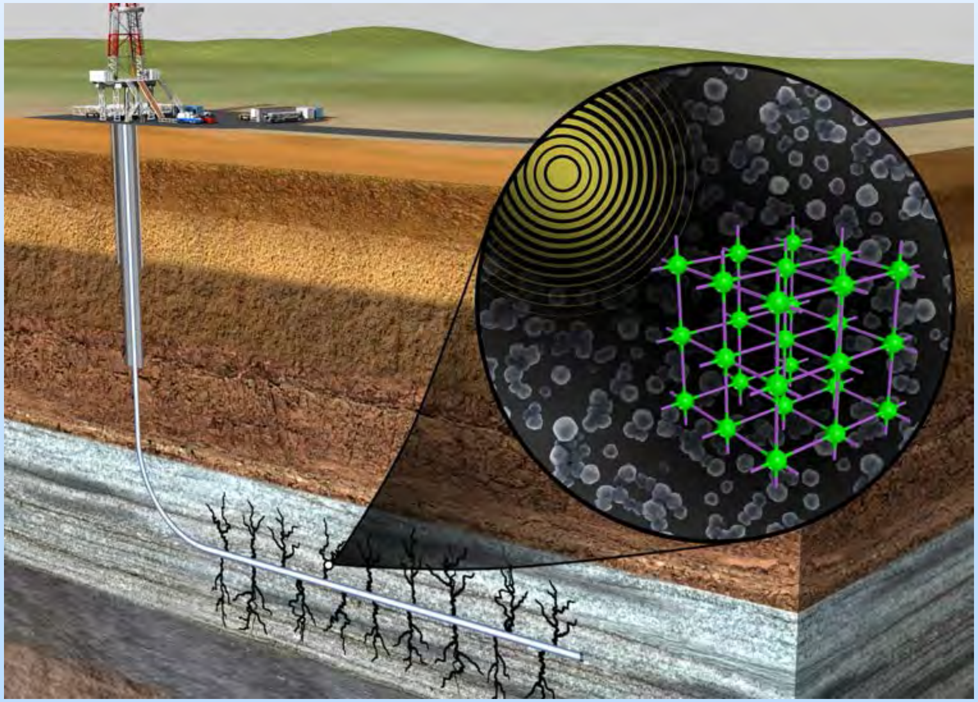
- Task 1 – Enhanced Monitoring Agents
  - 1.1 Synthesis of Acoustically-responsive Contrast Agents
    - Develop advanced functional materials for direct injection into permeable rock formations
    - Impedance tube measurements with sand/nanoparticle composites performance testing in a laboratory setting
  - 1.2 Laboratory-based Core Injection Experiments
    - Measure elastic properties of sandstone cores injected with contrast agent bearing nanofluids
    - Initiate core testing at subsurface pressure
  - 1.3 Numerical modelling of seismic wave propagation and reflections
    - Assist with injection strategy development and signal characteristics in model geologic systems
    - Parametrize model with core test measurements
  - 1.4 Field Test Development Plan

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



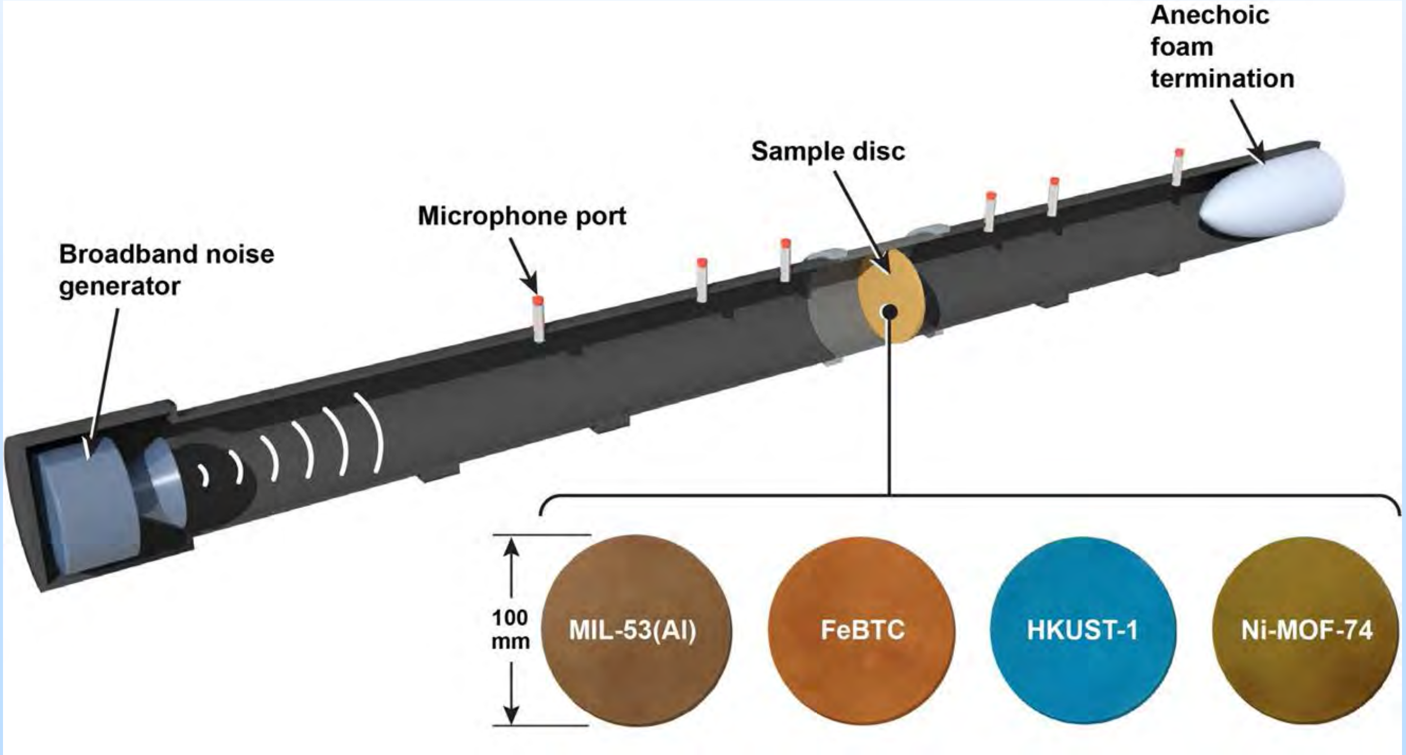
Transmission Loss Measurements

- Utilize impedance tube to measure acoustic properties
- Synthesized various acoustic absorbers (MOFs pressed into 100 mm-diameter discs
- Sound transmission loss (TL) of discs quantified
- TL results compared to the mass law of panel sound absorption

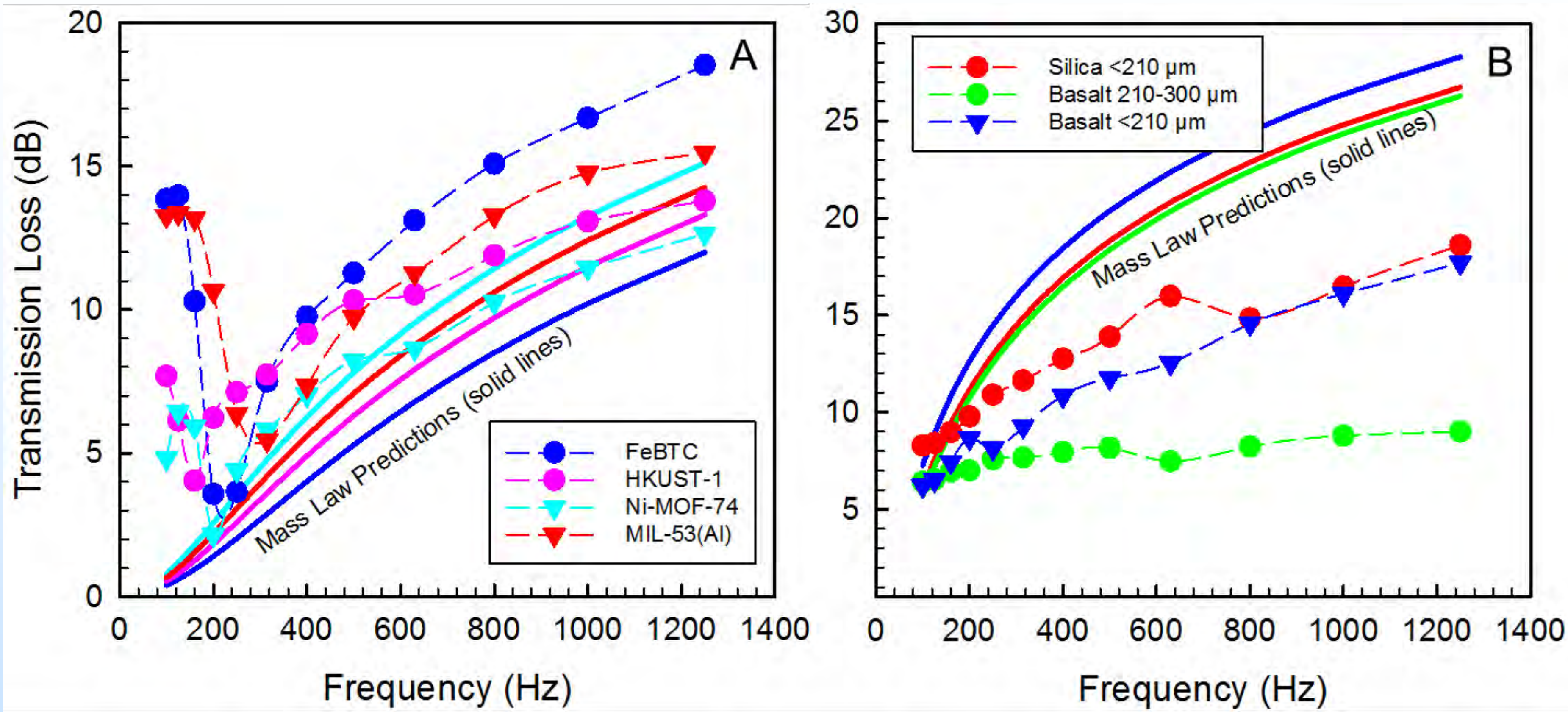
Mass Law

$$TL = 10log_{10}\left[1 + \left(\frac{\omega \rho_s}{2\rho_0 c}\right)^2\right]$$

ω=freq, $\rho_0 c$ is acoustic impedance of air, and p_s is the mass of the material per panel area

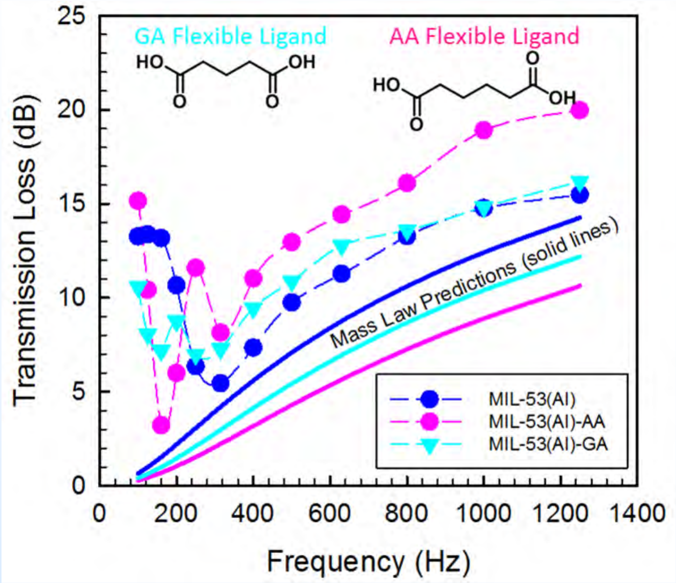


Acoustic anomalies with MOFs

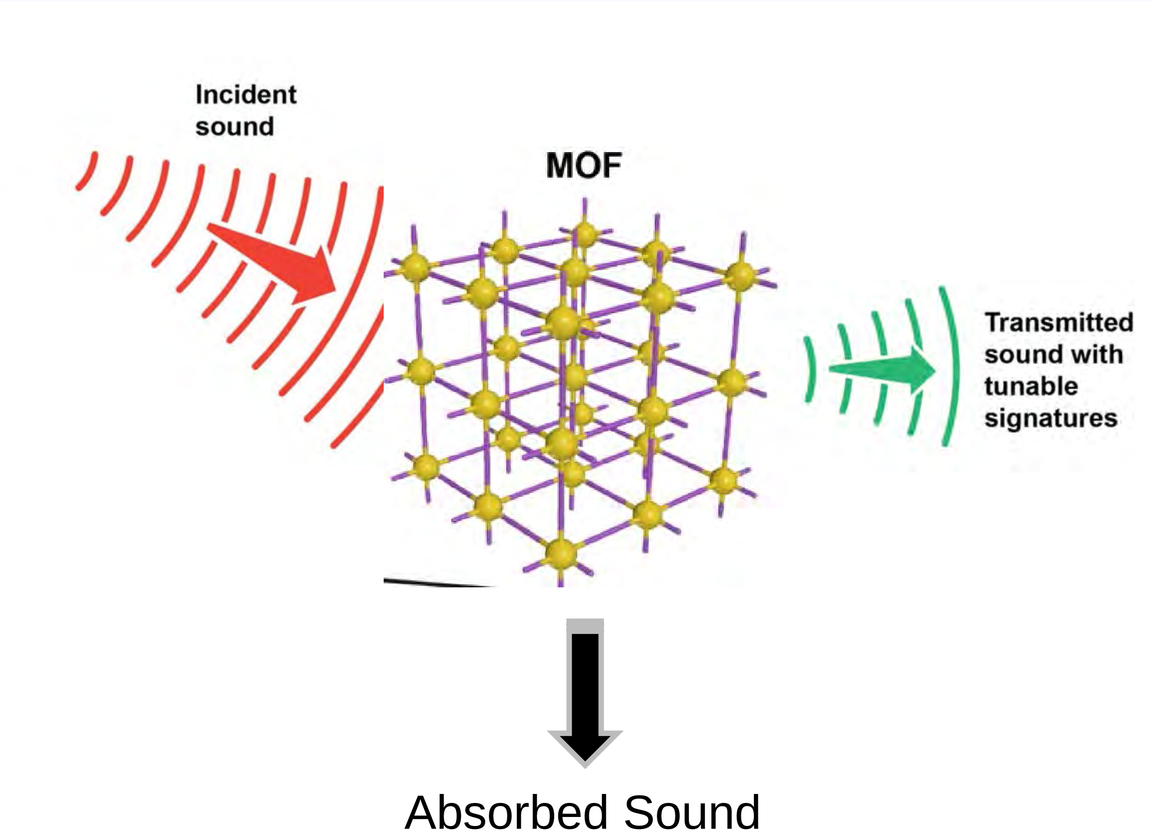


- Deviation from mass law by MOFs indicate unusual absorptive acoustic properties relative to natural rock materials
- MOFs also exhibit low frequency resonances

Acoustic Absorbers with Tunable Flexibility



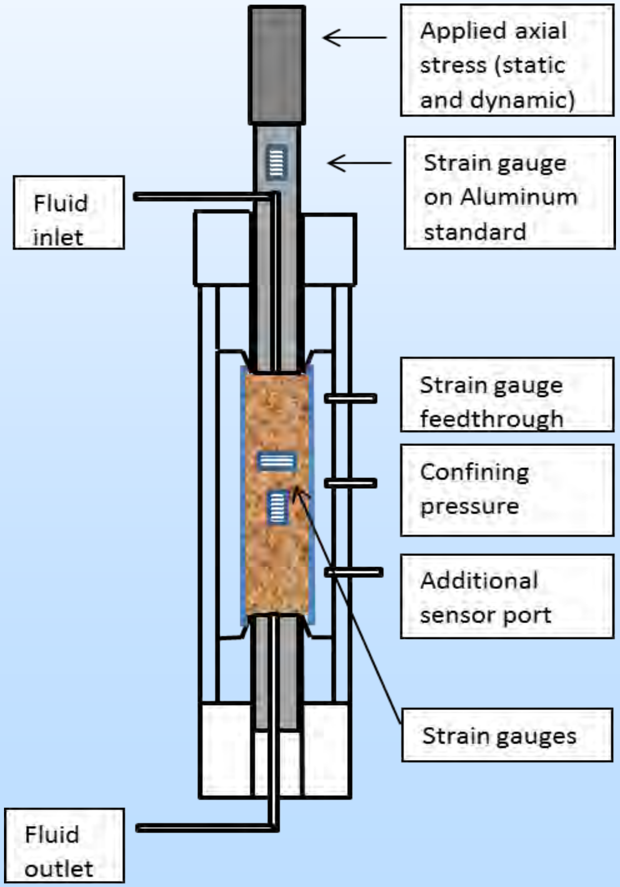
- Substitution of flexible ligands glutarate and adipate forms flexible framework MIL-53(Al) and new resonance peaks
- Flexible MOFs suggest potential to further outperform mass law behavior and tune signal characteristics for each application

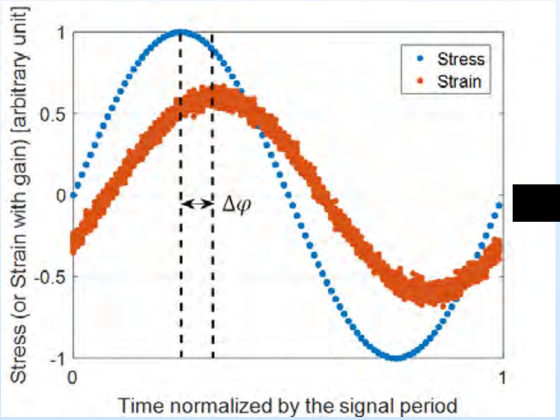


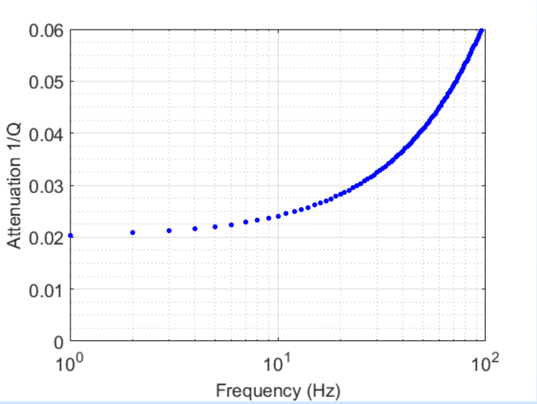
Seismic-Frequency Core Test System

Laboratory technique developed to measure seismic attenuation and velocity on rock core at relevant frequencies (0-100 Hz) under high confining pressure

- Impose known stress on sample and measure resulting strain (forced oscillation method)
- Both velocity and attenuation are key components in the wave propagation
- Phase shift between stress and strain provides information on attenuation
- Amplitude ratio provides velocity information (Young's Modulus)







Attenuation (Q^{-1}) is defined as: $\frac{1}{Q} = \tan(\Delta\varphi)$

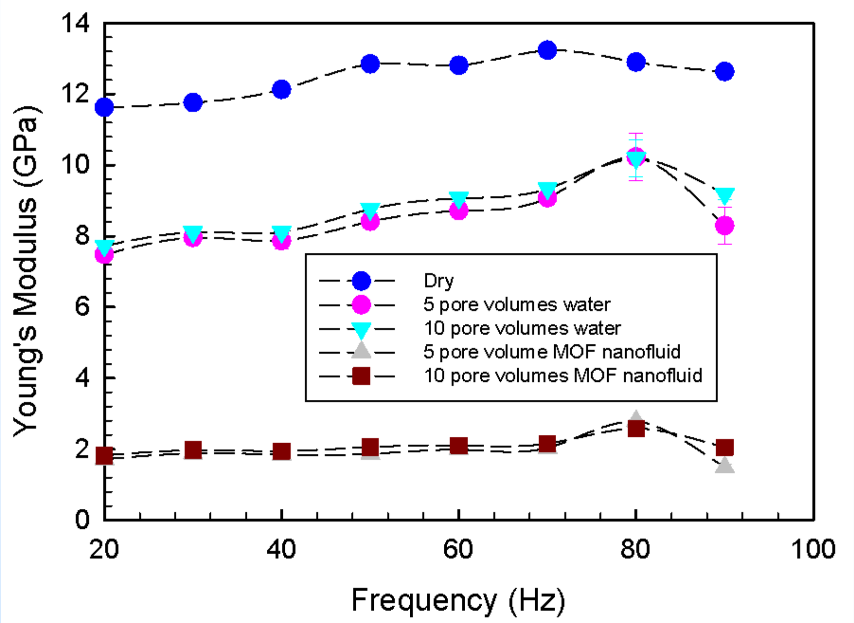
For small $\Delta\varphi$, $\frac{1}{Q} \approx \Delta\varphi$

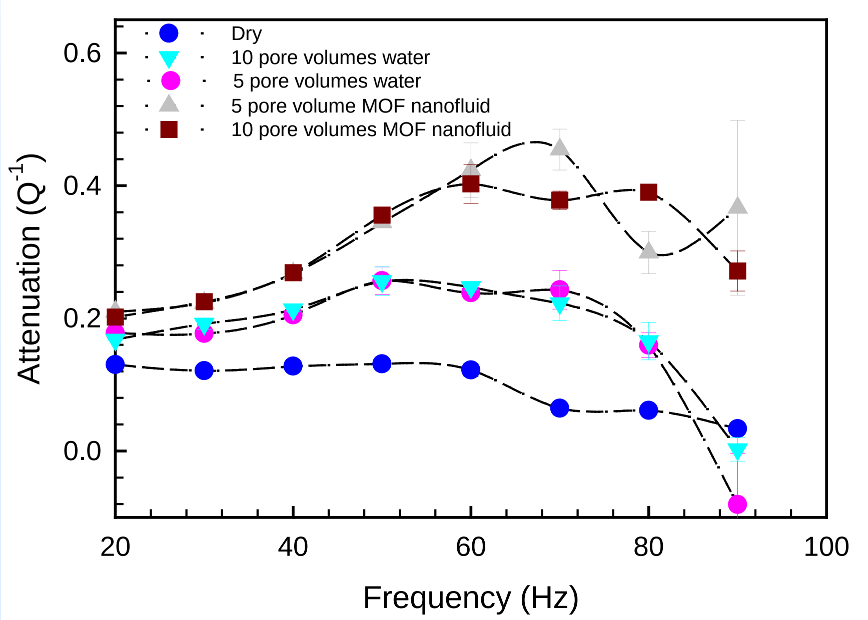
Effect of injectates (MOF nanofluids) on wave propagation behaviors (e.g., refraction, reflection, dissipation and attenuation)

Evidence of Seismic Properties Being Altered in Berea Sandstone Containing MIL-101(Cr) Nanofluid

Elastic properties (Young's modulus) of Berea SS:

- Dry core: near constant value of ~12 GPa
- Water-saturated core: ~6-8 GPa with an observable increases at higher frequencies
- MOF nanofluid: Anomalous decrease due to wettability (2 GPa) modification at rock-water interface





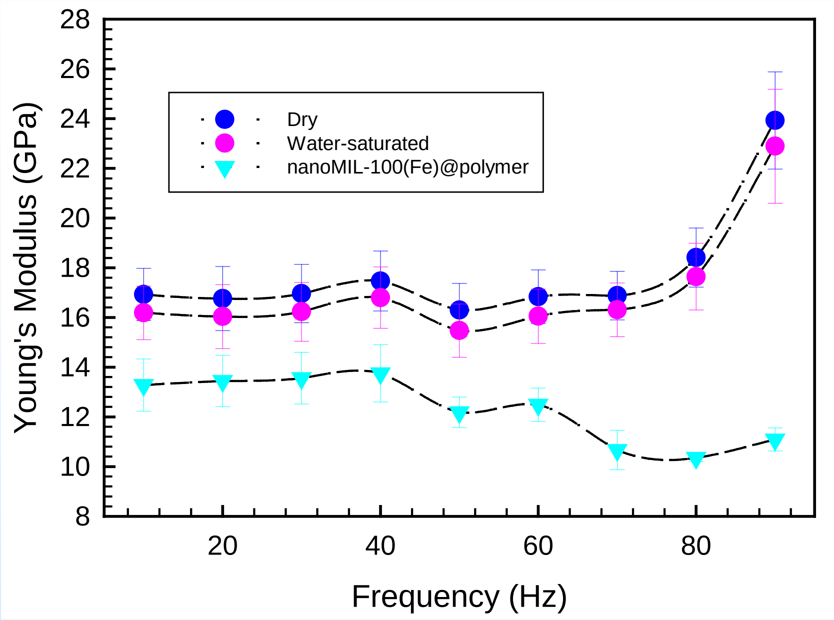
Seismic attenuation in Berea SS:

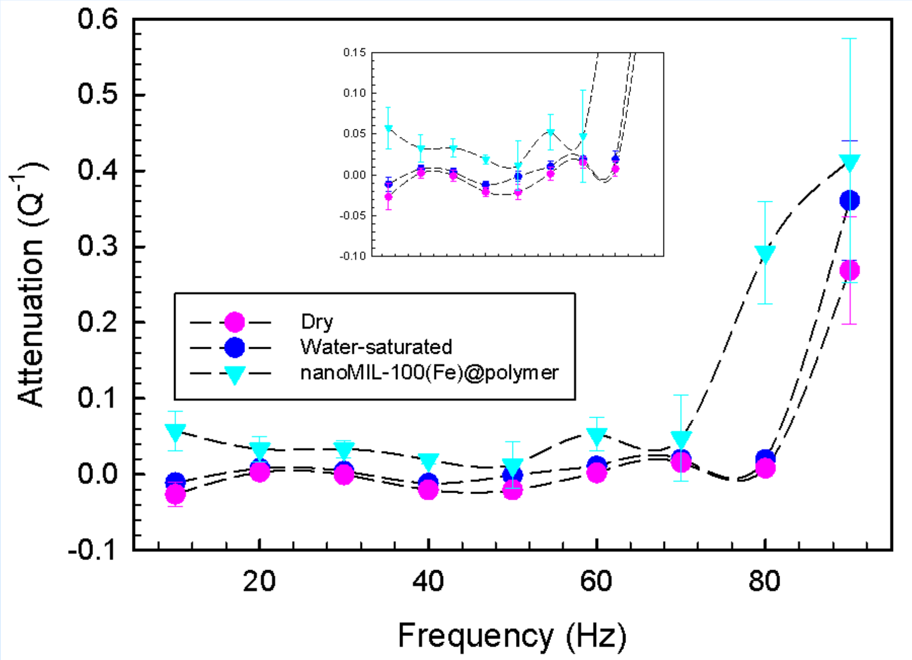
- Dry core: near linear response up to 60 Hz
- Water-saturated core: slightly higher response (0.8-0.22 radians)
- MOF nanofluid: Attenuation increases relative to other measurements, especially at >50 Hz

Berea Sandstone Core Tests with MIL-100(Fe) Nanofluid

Mechanical property (Young's modulus) of Berea SS:

- ~3 GPa decrease from 10-40 Hz in Young's Modulus when ~5 pore volumes of polymer-coated MIL-100(Fe) is injected into the Berea SS core
- Influence of contrast agent is most pronounced above 60 Hz





Attenuation measurably increases due to nanofluids

Results for hybrid MOF-polymer nanofluid promising for contrast agent applications

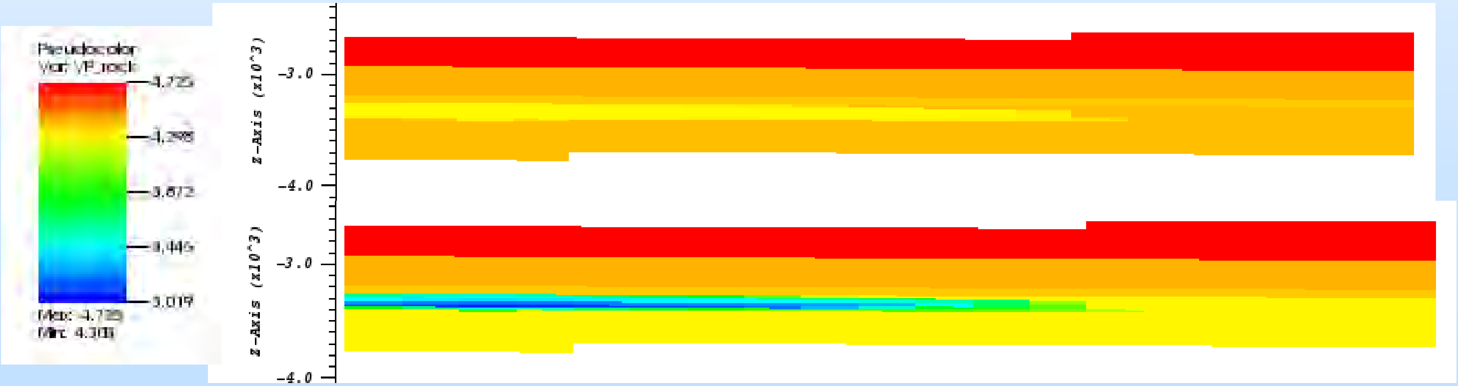
Ongoing and Future Work

Continued synthesis and testing of high-performance contrast agent nanofluids

- Zeolitic framework nanoparticles have high surface area (960 m^2/g) and are stable up to 560 ° C
- Preliminary results indicate elevated transmission loss and colloidal behavior

Simulations parameterized by core test data

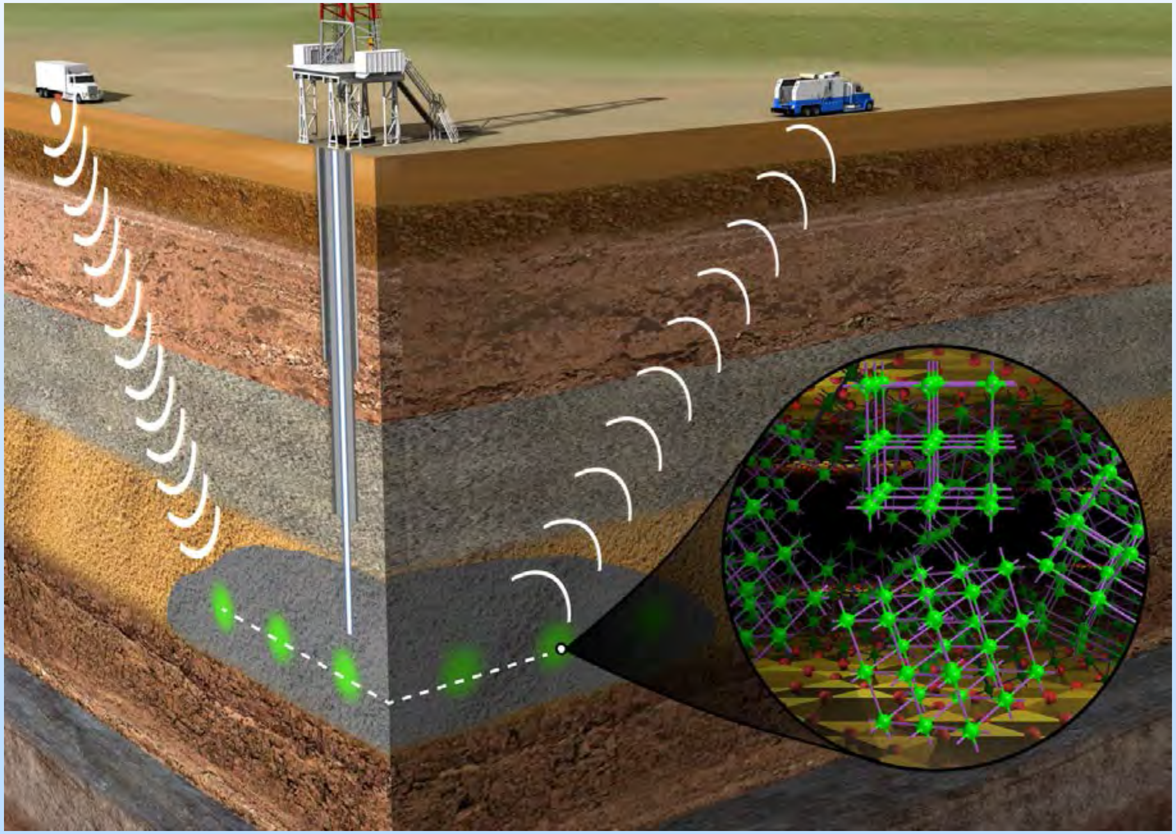
- Development of multiphase geophysical simulations to evaluate contrast agent performance in the subsurface
- Initiate field test plan based upon seismic simulations



Accomplishments to Date

- Continued to synthesize and screen candidate MOFs for core-scale testing
- Identified MOFs as acoustic metamaterials
- Successfully completed seismic core testing with two MOF nanofluids
- Initiated numerical simulations based on laboratory measurements

Realizing Emergent Properties of Acoustic Metamaterial Nanofluids in the Subsurface



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

#	Type [1]	Regular or Stretch [2]	Expected Completion Date	Description
1	Progress	Regular	12/31/2017	Identify two to three most promising materials in subtask 1 for transfer to subtask 2
2	Progress	Regular	3/30/2018	Initiate core flood tests (atmospheric conditions) using the linear variable displacement transducers (LVDT) apparatus with a Berea Sandstone and nanomaterials identified in subtask 1. This activity will focus on utilizing the new core testing apparatus and refining the core preparation protocol for use at reservoir pressures. Results from this activity will be transferred to simulations subtask.
3	Progress	Regular	6/30/2018	Initiate core flood testing at realistic reservoir pressure with a Berea Sandstone and nanomaterials identified in subtask 1. Results from this activity will be used in Q4 for simulations.
4	SMART	Stretch	12/31/2018	Initial seismic response modeling activity shows emplacement geometry and nanoparticle properties required to double signal-to-noise ratio in seismic waveform response.
5	Progress	Regular	12/31/2019	Subtask 1 completes development and testing of optimized acoustic contrast nanomaterials.
6	Progress	Regular	3/30/2020	Final set of acoustic and core property data collected and transferred to seismic imaging subtask

Bibliography

- Miller, Q.R.S., Schaef, H.T., Nune, S.K., Jung, K.W., Burghardt, J.A., Strickland, C.E, Martin, P.F., McGrail, B.P. (**2018)**. "Injectable Acoustic Metamaterial Nanofluids for Geophysical Monitoring", *in prep*
- 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, *submitted*
- 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

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Gantt Chart

Detailed Schedule

FY 2015-FY 2016: July | Aug | Sept | Oct | Nov | Dec | Jan | Feb | March | April | May | June

#	Task Name Project Management	Start	Finish
1	Manage Project	Jul-15	Jun-16
2	FY15 Q4 Report	Jul-15	Sep-15
3	FY16 Q1 Report	Oct-15	Dec-15
4	FY16 Q2 Report	Jan-16	Mar-16
5	FY16 Q3 Report	Mar-16	Jun-16

#	Milestone Description	Milestone Date
6	Develop a high-pressure, in situ spectroscopic capability for quantifying sorption of methane onto organic-rich shales. Experiments will be conducted to measure methane retention on natural shales at representative reservoir conditions. This work will include a series of experiments where pure kerogen is exposed to scCO2 at relevant reservoir conditions to obtain partition coefficients.	Sep-15
7	Conduct a series of pressurized FTIR titrations coupled to in situ XRD experiments using cation saturated montmorillonites and natural shale gas core samples to establish mineral structural changes and gas sorption behaviors occurring in CH4/CO2 mixtures as a function of dissolved water content. Experimental results will be used in computational geochemistry studies to obtain mechanistic processes dominating CH4/CO2 exchange under realistic reservoir conditions. The final outcomes will be contributions to the development of optimum injection strategies and idealized in situ conditions for maximizing CH4/CO2 exchange rates in depleted shale gas reservoirs.	Sep-15
8	Complete isotopic measurements on carbonate material removed from sidewall cores collected from the Basalt Pilot Well and compare results to those carbonates known to occur naturally within the basalt flows. The outcome will be documented reported in the quarterly report.	Dec-15
9	Conduct a series of pressurized Atomic Forced Microscopy (AFM) experiments that capture carbonation of a pure mineral phase in the presence of scCO2 and water. These measurements have the potential of providing diagnostic information on carbonate nucleation, meta-stable intermediate transitional phases, and crystal growth rates in occurring in a wet scCO2 fluid.	Dec-15
10	Complete acoustic velocity measurements for CO2 based nanofluids systems using pressurized low-frequency dynamic geomechanical techniques. Results of these experiments will help define materials suitable for additional testing.	Mar-16
11	Summarize findings associated with the Wallula Basalt Pilot well into a manuscript for submission to a high impact peer reviewed journal. These finds will include comparisons between down hole logging surveys measuring pore fluid saturation, thermal impacts of the injected CO2 on formation temperature, and comparison 13C and 18O values between the injected fluid, groundwater samples, well cuttings, and those carbonate nodules identified in side wall cores and natural occurring carbonates.	Mar-16
12	Conduct a series of in situ FTIR and XRD experiments to characterize thin water film development and carbonation of important basalt mineral silicates (i.e. pyroxene, fayalite, and microcline etc.). Data generated from these experiments will complement our data set on forsterite and plagioclase minerals. We will utilize computation geochemistry to identify key reaction mechanisms that 1) drive water film development and 2) control carbonation. Outcomes from this study will be incorporated into reservoir models to obtain better prediction of CO2 storage in basalt formations.	Jun-16
13	Conduct pre-closure geochemical characterization activities consisting of wireline geophysical logs and wireline side-wall coring, and laboratory characterization/analysis of the core samples. The results will include the compilation of groundwater characterization data which will be summarized in quarterly reports.	Jun-16

Project: Capture and Sequestration Support Services

Task — Milestone — Phase — Quartly Report