New Imaging and CO_2 Storage Technologies for Unconventional Subsurface Reservoirs

Project Number 70066

PI: Quin Miller

Pacific Northwest National Laboratory

U.S. Department of Energy

National Energy Technology Laboratory
Carbon Management Project Review Meeting
August 15 - 19, 2022

Presentation Outline

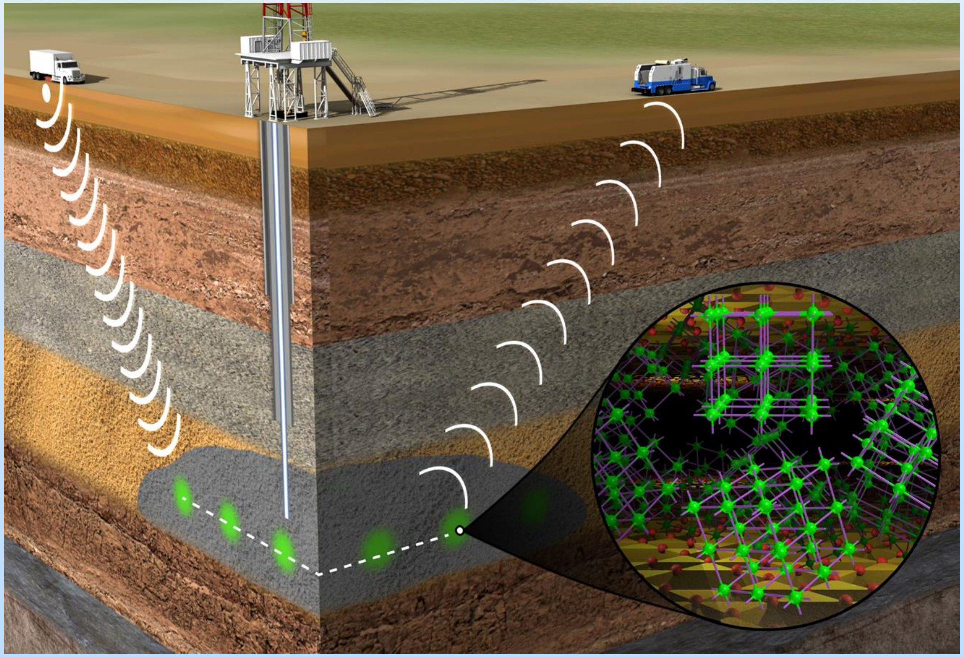
- Goals and Objectives
- Project Overview
- Technical Discussion
- Accomplishments to Date
- Synergy Opportunities
- Project Summary
- Appendix (Organization Chart, Gantt Chart, and Bibliography

Enhanced Contrast Agents for CO_2 Monitoring

Problem Statement: Current monitoring techniques for detecting and surveying injected CO_2, other fluid mixtures, and fracture networks suffer from low detection sensitivity and limited volumetric resolution

- Engineering nanomaterials for subsurface injection
- Dispersion injectates and formation water to form colloidal nanoparticle suspensions (nanofluids)
- Detection through conventional seismic imaging

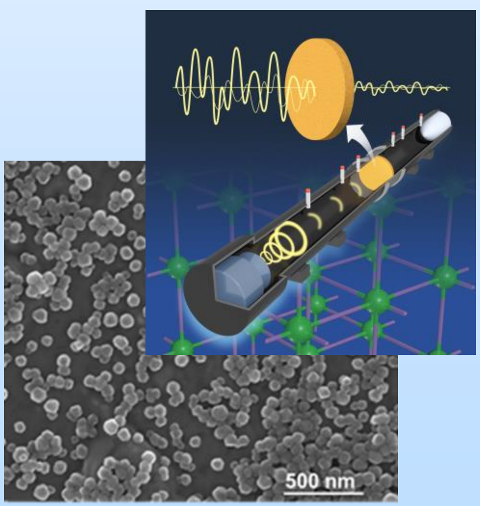
Goal: Develop contrast agents for enhanced time-resolved monitoring/mapping of subsurface fluids and structures, including injected CO_2

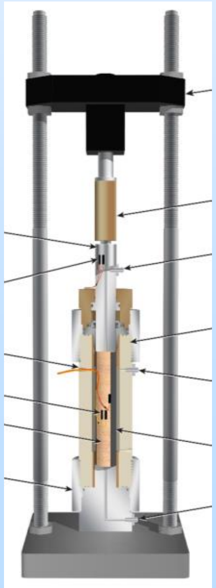


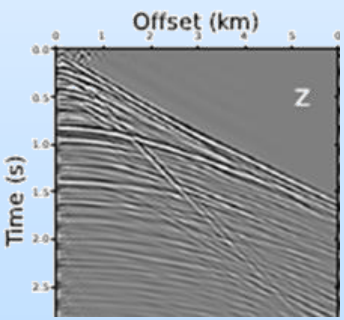
Project Overview

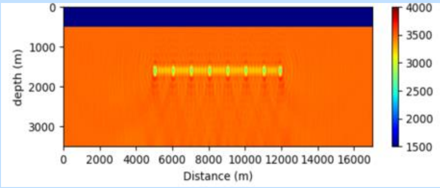
- Funded through FY23, $330k
- Enhanced Monitoring Agents
  - 1.1-1.2 Synthesis and Stability Testing
  - 1.3-1.4 Laboratory-Based Core Test Experiments
  - 1.5 Predictive Seismic Simulations
  - 1.6 Field Test Plan Development

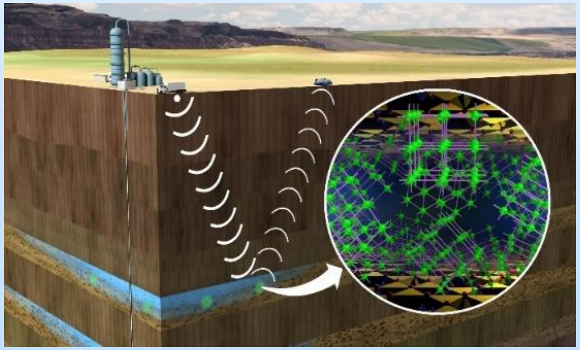
Synthesis ⟷ Experiments ⟷ Simulations ⟷ Field Test Plan







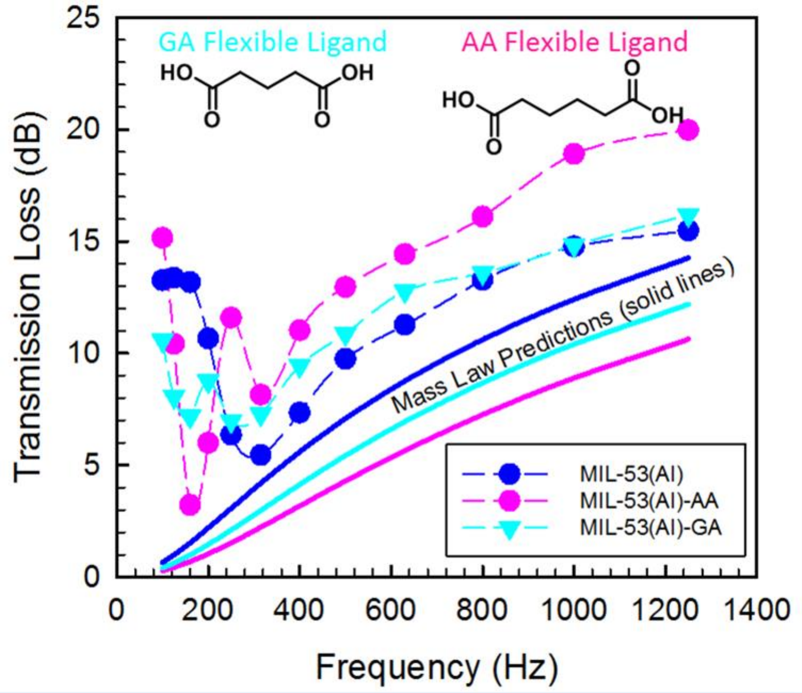




MOFs are Acoustic Metamaterials that Influence Elastic/Anelastic Properties of Rocks

Applications/Significance/Novelty

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



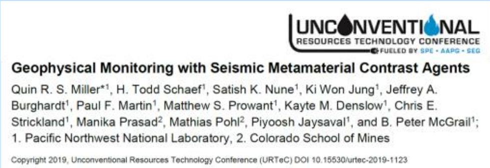
- Injectable nanoparticles with ultra-high surface area and tunable flexibility
- Metal-organic frameworks have anomalous low-frequency sound attenuation properties: Acoustic Metamaterials
- Laboratory geophysical experiments indicate MOF nanofluids alter the elastic and anelastic properties of fluid-bearing rocks (Young's modulus and Attenuation)
- These microporous materials may be used as acoustic contrast agents for better resolving subsurface fluids and structures


ACS APPLIED MATERIALS & INTERFACES — Letter

Cite This: ACS Appl. Mater. Interfaces 2018, 10, 44226–44230 — www.acsami.org

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

Quin R. S. Miller,*,† Satish K. Nune,‡ H. Todd Schaef,† Ki Won Jung,‡,§ Kayte M. Denslow,⊥ Matthew S. Prowant,⊥ Paul F. Martin,‡ and B. Peter McGrail‡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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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ELSEVIER — Available online at www.sciencedirect.com — ScienceDirect — Energy Procedia

Energy Procedia 114 (2017) 3764 – 3770

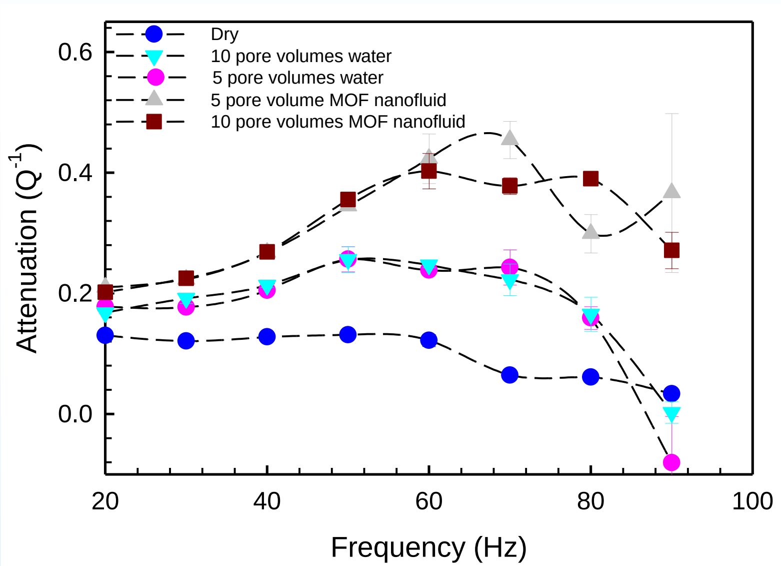
13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

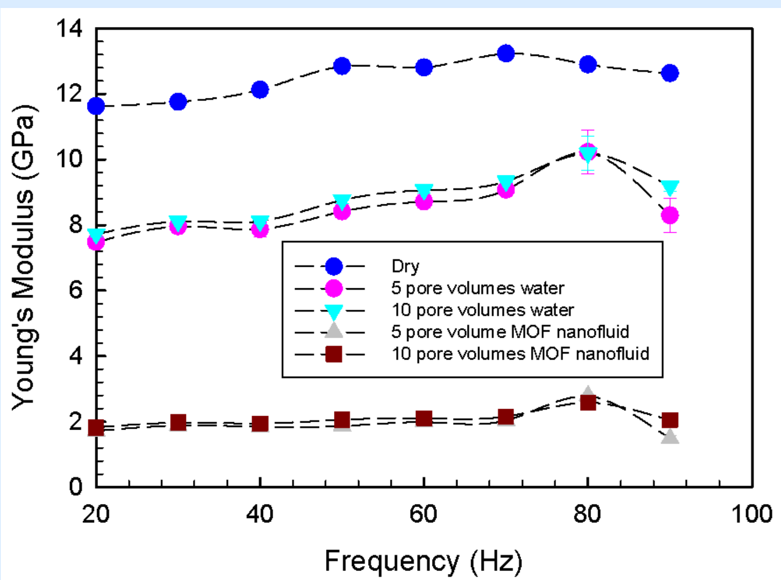
Injectable Contrast Agents for Enhanced Subsurface Mapping and Monitoring

H. Todd Schaef*, Chris E. Strickland, Ki W. Jung, Paul F. Martin, Satish K. Nune, John S. Loring, and B. Peter McGrail

Pacific Northwest National Laboratory, P. O. Box 999, Richland, Washington 99352

MOFs are Acoustic Metamaterials that Influence Elastic/Anelastic Properties of Rocks





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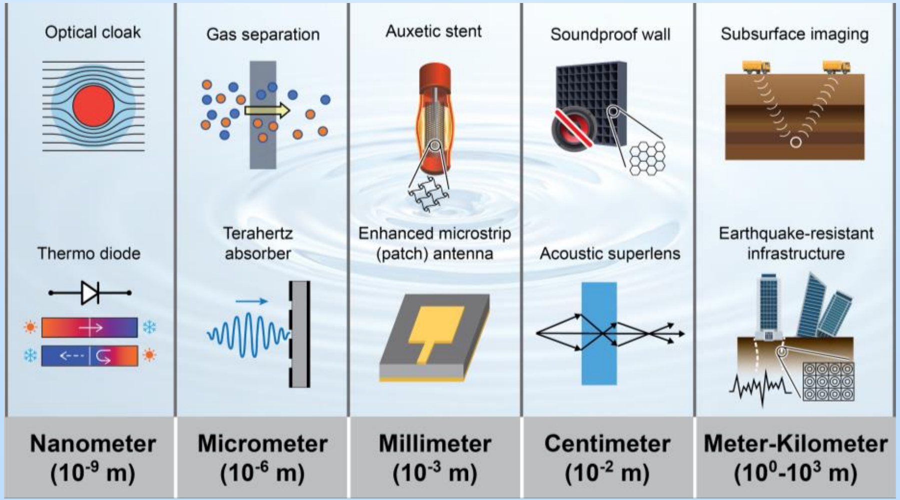
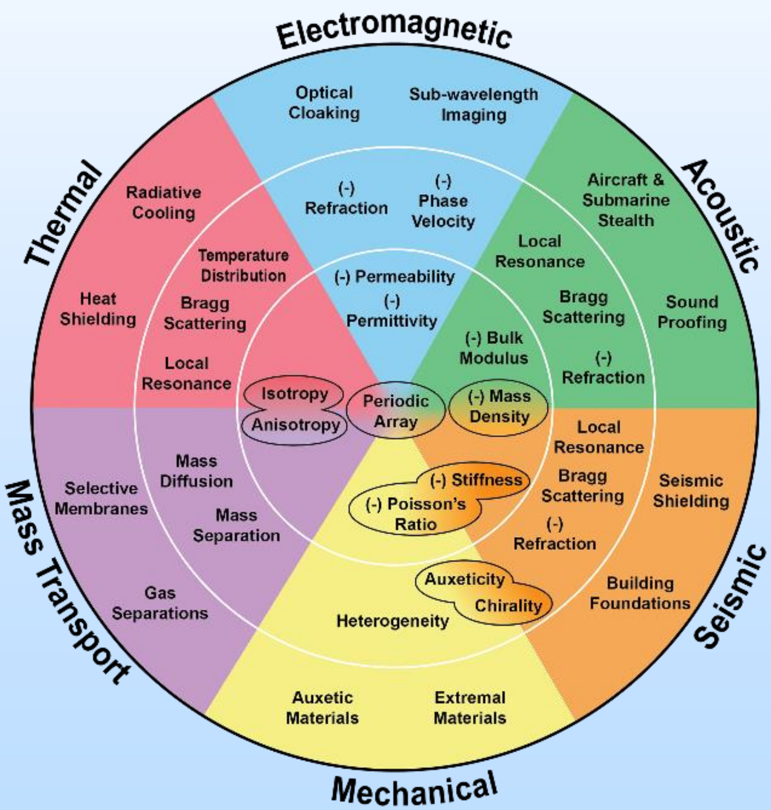
Extending Principles of Metamaterial and Design to the Subsurface

Metamaterials are comprised of composite media with periodic subwavelength structure engineered to exhibit unique optical, magnetic, or acoustic properties etc.

Composed of unit cells that work collectively to produce unusual, unique physical properties not found in natural materials or traditional composite materials, used to manipulate propagation of waves

- Develop acoustically responsive contrast agents
- Develop methods for generating periodic subsurface structures
- Driving forward the emerging field of seismic metamaterials to enhance monitoring of subsurface fluids and structures
- Multiple length scales key to our monitoring technology

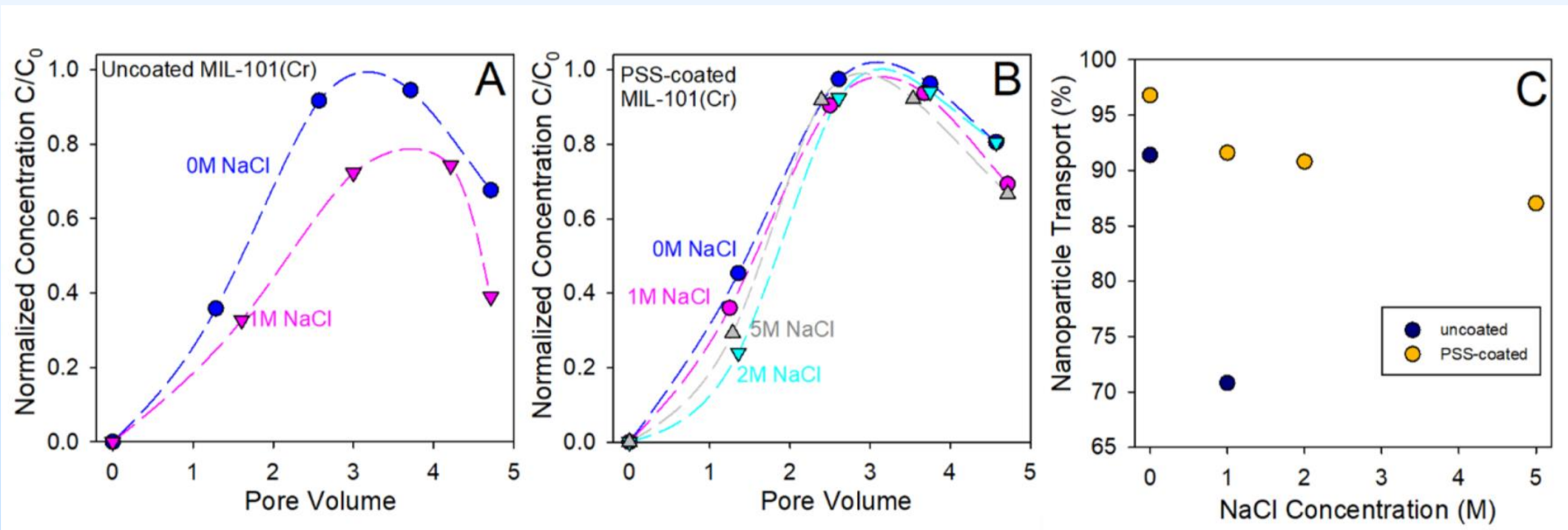


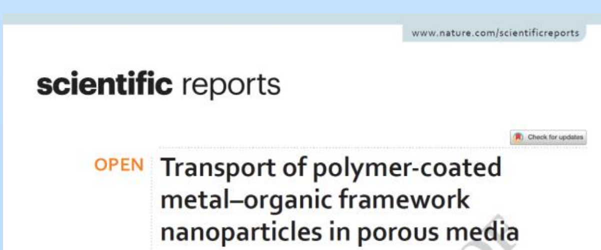


Holliman et al. 2022, Revised Manuscript Under Review

Polymer Coatings Enhance Colloidal Stability and Transport

- Polymer coatings may be used to tailor nanofluid properties for different reservoir types
- PSS-70K, poly(sodium 4-styrenesulfonate) was the best candidate due to surface charge, zeta potential magnitude, radius, and low retention in column
- Polymer (PSS) coatings reduced retention of nanoparticles in the column experiments relative to DI water conditions
- Breakthrough curves for MOF nanoparticle transport are similar due to PSS coatings
- Only small decreases observed in nanoparticle transport with increasing ionic strength
- Repulsion from silica surfaces and other nanoparticles promotes efficient transport

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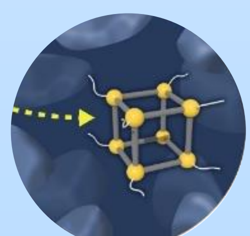
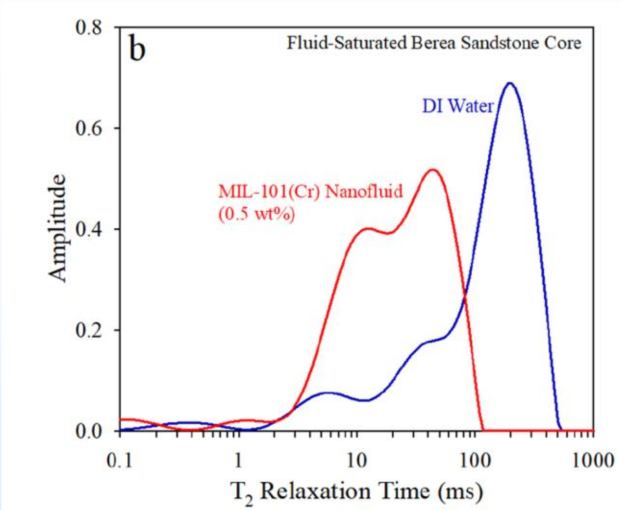
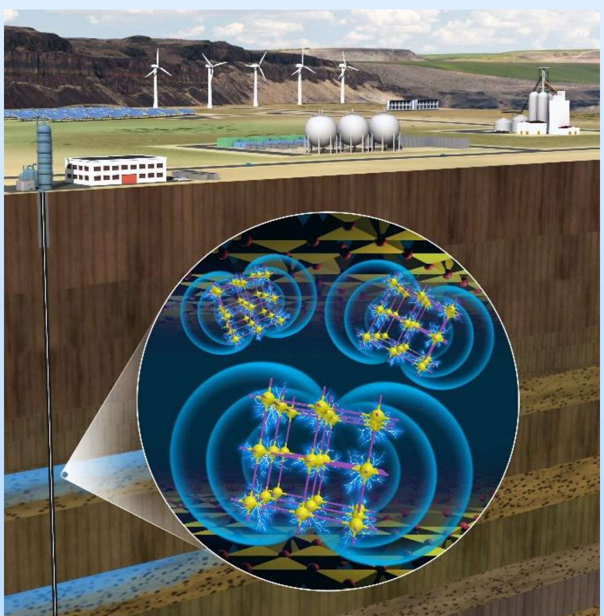
OPEN Transport of polymer-coated metal–organic framework nanoparticles in porous media



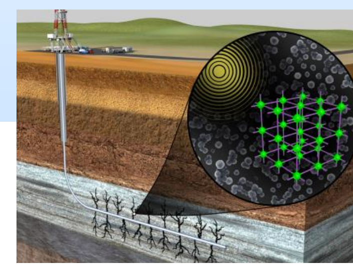
Nune et al. Sci. Rep. 2022, In Press

Seismic Contrast Agent Injectates also Influence Near-Wellbore Geophysical Signatures





- Injectable nanoparticles also exhibit distinct NMR and electrical signatures
- Three prototypical MOFs investigated
- Multimodal signatures complement the seismic contrast agent application with monitoring of near-wellbore processes
- Key result involved NMR measurements of contrast agent nanofluid in Berea sandstone core
- Manuscript co-lead by PNNL and CSM (Pohl, Livo, Prasad)



ACS APPLIED MATERIALS & INTERFACES

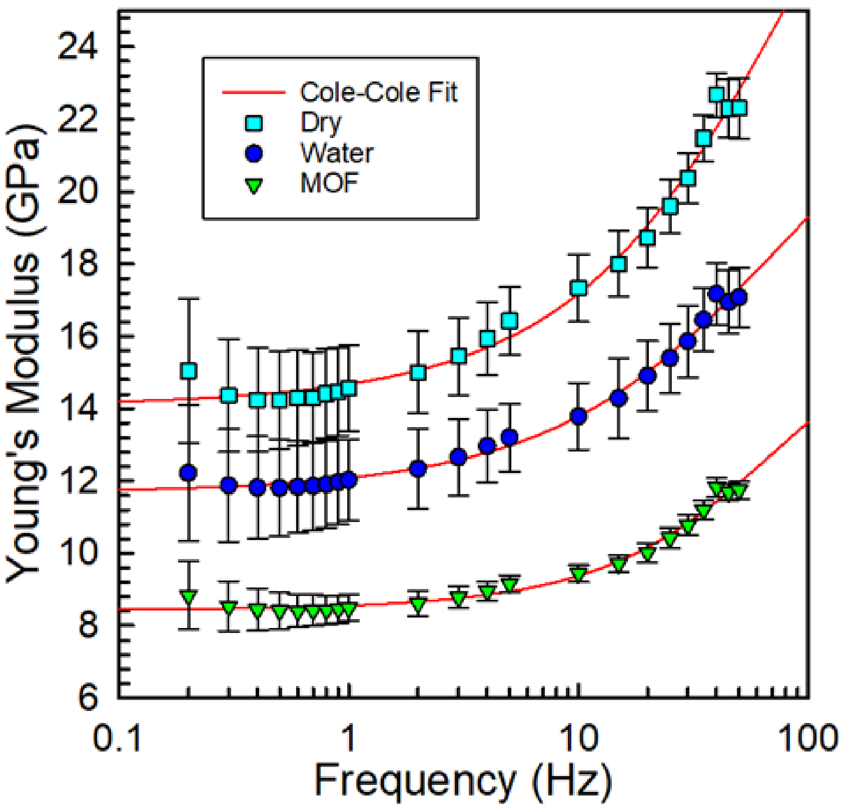
www.acsami.org Research Article

Porous Colloidal Nanoparticles as Injectable Multimodal Contrast Agents for Enhanced Geophysical Sensing

Quin R. S. Miller,* Mathias Pohl,* Kurt Livo, Hassnain Asgar, Satish K. Nune, Michael A. Sinnwell, Manika Prasad, Greeshma Gadikota, B. Peter McGrail, and H. Todd Schaef

Decrease in Young's Modulus Observed at Lower Frequencies

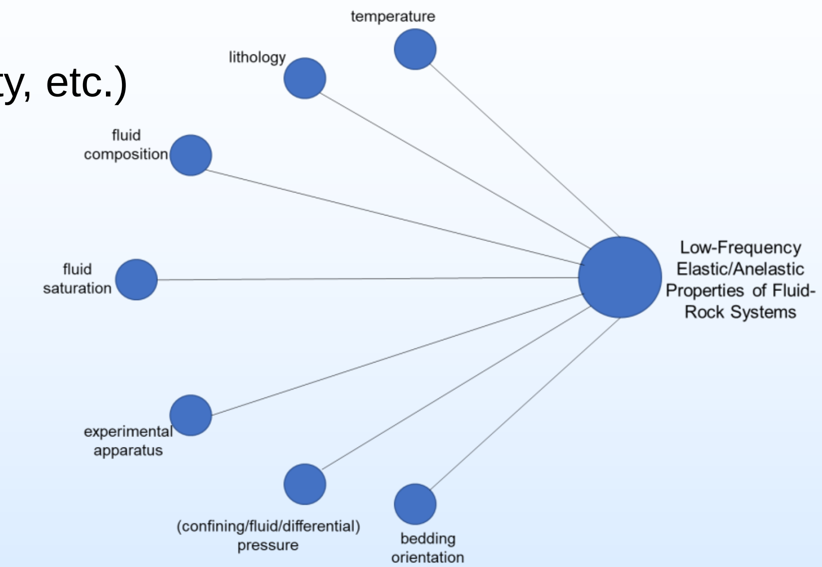
- New LVDT and SG hybrid core test system
- Forced oscillation apparatus for measuring the elastic properties (Young's modulus, *E*) and extensional attenuation (Q^{-1}_E) in Berea sandstone
- Young's modulus measurements of Berea sandstone for three different conditions: dry, complete water saturation (81 pore vols.), and after 16 pore volumes of 0.5 wt% MIL-101 MOF nanofluid.
- Extended frequency range to 0.2-10 Hz
- Data fit to Cole-Cole Relaxation model
- Data transferred to Simulation task to predict attenuation in a reservoir



- 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
- Wettability alteration?
- Suggests non-porous engineered materials may be used as contrast agents

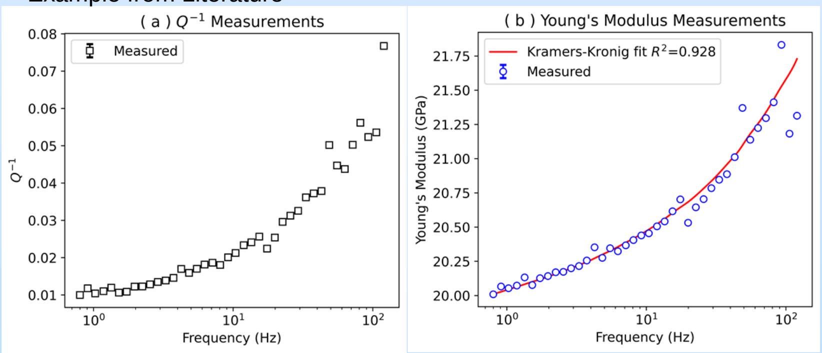
Towards Predictive Frameworks for Low-Frequency Fluid-Rock Interaction

- First quantitative analysis of broad forced oscillation literature via the Kramers-Kronig (K-K) relations to verify the causality between E and Q^{-1}_E
- Wide range of experimental conditions in literature:
  - Rock type & attributes (i.e., porosity, permeability, etc.)
  - Saturating fluid (e.g., $scCO_2$, oil, brine)
  - Differential pressure
  - Boundary conditions (drained or undrained)
  - Frequency
  - Temperature



- Of the 286 datasets analyzed via the K-K relations, 87 (30.4%) produced R^2 fits of ≥0.8 or greater
- Indicates relationship between attenuation and dispersion for fluid-bearing rocks is more complex than previously thought, new models needed that encompass overlapping mechanisms, including the effects of nanofluid injectates
- Highlights gaps in literature (e.g. basalt)
- Ongoing analyses of the broad training dataset will be used to parameterize predictive geophysical models that supplement our experimental campaign
- FY23 Manuscript milestone planned
- See Tuesday Poster Session: Jade Holliman

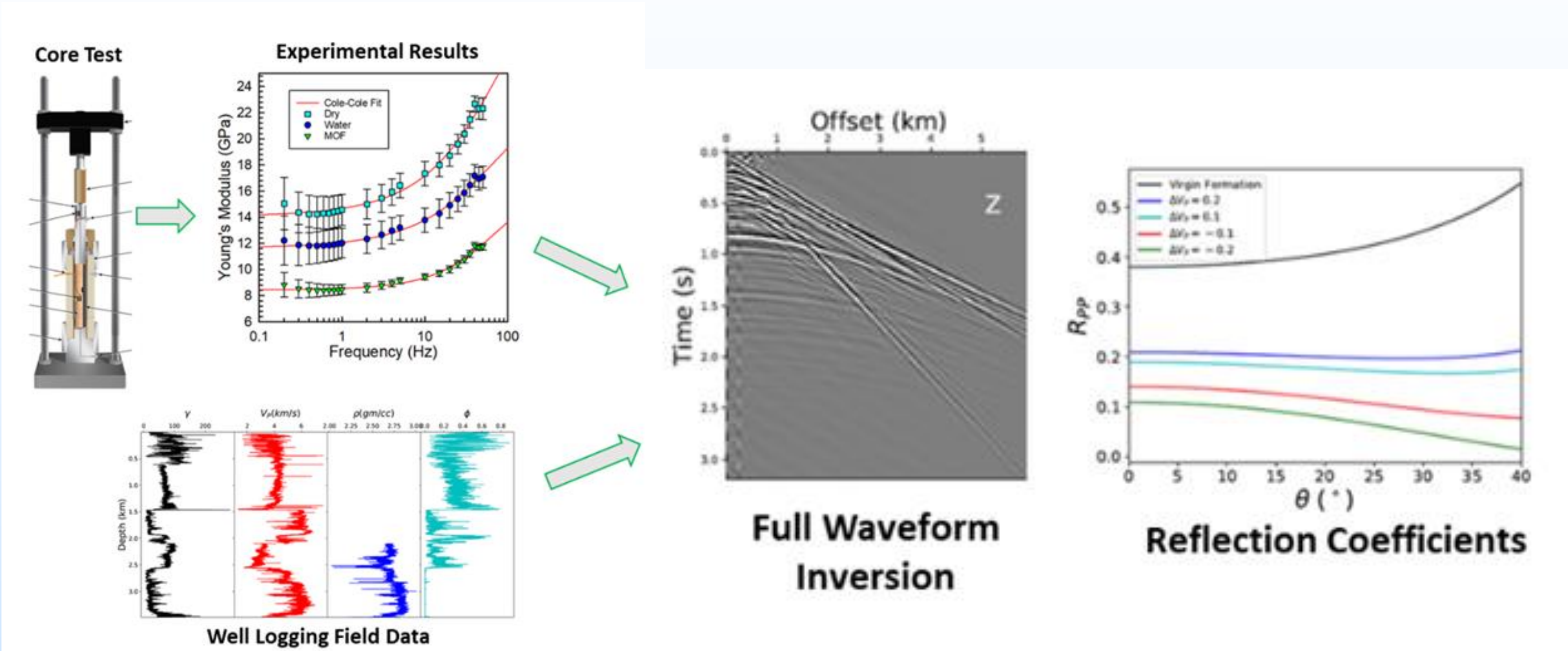
Example from Literature



Q^{-1}_E and *E* for a water-glycerin-saturated Berea sandstone measured at a differential pressure of 9.86 MPa (Tisato et al. 2021)

Forward Seismic Modeling

Forced oscillation testing of injectable contrast agent nanofluids used to parameterize forward seismic modeling



- Predictive seismic model describes changes to P (primary, compressive)-waves and S (secondary, shear)-waves.
- Parameterized by laboratory experiments and a real geologic setting:
- Well log data from a Utica Shale play with was used for the seismic modeling due to the presence of a sandstone (reservoir) bed overlain by caprock shale layers.
- AVA for the top and bottom shale/sandstone interfaces show how MOF’s in the sandstone pore space influence reflection coefficients of seismic waves, a measure of energy reflected off an interface.
- PP-wave reflection coefficients are sensitive to the presence of MOF-bearing fluids.
- Combined experimental and simulation results will be reported in FY22 Q4 manuscript milestone (Behura and Miller et al.)

Looking Ahead to Future Testing/Development/Commercialization

- Experimental data and simulations to be summarized in Field Test Plan key to enabling future permitting and injection-strategy design
- Commercial pathways to getting MOF nanofluids produced
- We are actively looking for a field test partner for injection and seismic monitoring pilot field study
- Field test site synergy with future phases of:
  - Regional Partnerships (CUSP)
  - ARPA-E (Rio Tinto)
  - CarbonSAFE
  - DAC Hub

Accomplishments to Date

- First to examine the acoustic properties of MOFs, demonstrated that they are acoustic metamaterials
- Identification of best-performing polymer-coated MOF nanoparticles for colloidal stability and transport
- Revealed that acoustic nanoparticles have potential for near-wellbore multimodal sensing also due to distinct NMR and electrical signatures
- Parameterized predictive field-scale seismic simulations with low-frequency core test results, demonstrated influence of amplitude and attenuation
- Brought updated low-frequency LVDT hybrid core test capability online
- Synthesis of stable injectable colloids
- Predictive model development from KKR and C-C literature analyses
- Placing this carbon storage monitoring technology in the broader context of seismic metamaterials
- Paper under review at Materials Advances (Holliman et al. 2022)
- Paper in press at Scientific Reports (Nune et al. 2022)
- Paper published at ACS Applied Materials and Interfaces (Miller et al. 2022)

Synergy Opportunities

- Technology we are developing is tunable for different lithologies and fluid compositions
- Contrast agent approach may be used with conventional seismic imaging technologies
- Injection at a field location or test bed may be monitored with multiple approaches, from far-field to near-wellbore technologies

Synergy Opportunities

Mission Innovation CCUS Workshop Report

Enhanced Caprock Monitoring

- PRD S-1, S-4, and CC-2
- PRD CC-1: Integrating Experiment, Simulation, and Machine Learning across Multiple Length Scales to Guide Materials Discovery and Process Development

Mapping of Subsurface Structures

- Spatial resolution enhancement for fluid interfaces and fracture networks
  - PRD S-1, S-4, U-9, and CC-2
  - PRD S-6: Improving Characterization of Fault and Fracture Systems

Wellbore Integrity Monitoring

- Incorporation of acoustically-active materials for wellbore infrastructure monitoring
  - PRD S-9: Establishing, Demonstrating, and Forecasting Well Integrity

Deployment in Reactive Storage Reservoirs

- Mafic and ultramafic reservoirs targeted by ARPA-E and FECM

Project Summary

– Key Findings: Nanofluid injectates operate at seismic frequencies, are stable and mobile in porous geologic media, and act as multimodal contrast agents for seismic surveys and wellbore monitoring
– Disruptive approach to tracking subsurface CO_2 catalyzed by new metamaterial insights
– Next Steps: FY23 Tasks
  - Task 1: Contrast Agent Design and Stability Testing
  - Task 2: Core Test Experiments and Analysis
  - Task 3: Reservoir Analysis and Seismic Modelling
  - Task 4: Field Site Case Study

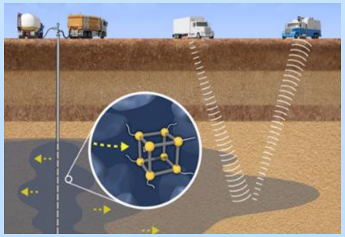
Publications

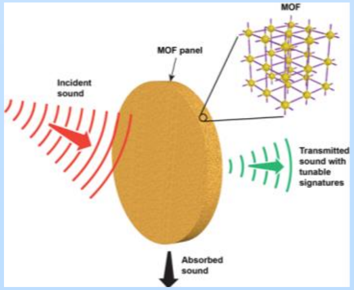
FY2022 Published, Accepted, or In Review

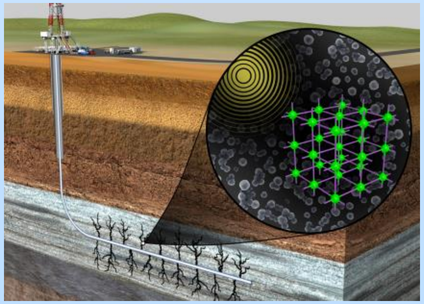
- Miller, Q.R.S., M. Pohl, K. Livo, H. Asgar, M.A. Sinnwell, H.T. Schaef, S.K. Nune, M. Prasad, G. Gadikota, B.P. McGrail. Metal-organic framework colloidal nanoparticles as injectable multimodal contrast agents for subsurface sensing. ACS Applied Materials and Interfaces, https://doi.org/10.1021/acsami.2c03187
- Nune, S.K., Q.R.S. Miller, H.T. Schaef, T. Jian, M. Song, D. Li, V. Shutthanandan, B.P. McGrail. Transport of Polymer-Coated Metal-Organic Framework Nanoparticles in Porous Media. Accepted at Scientific Reports. Preprint at https://doi.org/10.21203/rs.3.rs-1062071/v1
- Holliman, J.E., H.T. Schaef, B.P. McGrail, Q.R.S. Miller. Review of foundational and emerging directions in metamaterial research: Design, phenomena, and applications. Revisions In Review at Materials Advances.

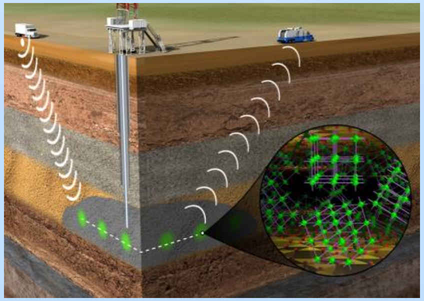
Other Key Project 70066 Publications

- 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., https://doi.org/10.15530/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 https://doi.org/10.1021/acsami.8b19249
- 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 https://doi.org/10.1016/j.egypro.2017.03.1506









Acknowledgements

This material is based upon work supported by the U.S. Department of Energy Office of Fossil Energy Carbon Management at PNNL through the National Energy Technology Laboratory, Morgantown, West Virginia.

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Posters Tomorrow

Jade Holliman
Post-Bach (Physics)

Mineralization and Metamaterial Contrast Agent Monitoring in Geologic Carbon Storage Reservoirs

Ross Cao
Post-Doc (Geology)

De-risk Basalt Reservoir via Regional Geologic Modeling and Simulation

Appendix

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

Benefit to the Program

- Derisking geologic carbon storage by enhancing monitoring 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

- The purpose of this project is to support NETL and the Office of Fossil Energy to develop technologies that efficiently and effectively characterize engineered subsurface systems. The proposed work aims to advance a new class of acoustically-responsive and injectable contrast monitoring agents that are specifically engineered for 1) mapping fracture networks associated with energy extraction processes, 2) improved delineation of storage reservoirs in multi-scale complex subsurface geological systems, and 3) enhancement of current near/far-field geophysical monitoring technologies.

Organization Chart

- PI: Quin Miller - responsible for leading experiments and overall subtask integration, science/technology goals, communication, and direction
- PM: Todd Schaef - subtask and budget management, science objectives and project goals
- Jade Holliman - core test experiments and analysis, metamaterials
- Pete McGrail - metamaterials
- Satish Nune - synthesis and stability testing
- Ting Bao and Jeff Burghardt - LVDT core test

Gantt Chart

Task	Milestone	Title	G/N	Begin	End
1.0		**Enhanced Contrast Agents for CO2 Monitoring**		0	12
1.1		*Synthesis of MOF Nanoparticles*			
	1.1.1	Complete selection of MOF materials for injection experiments in sub task 1.3.		2	2
	1.1.2	Down select polymer coatings and transfer to subtask 1.2 for testing		1	1
	1.1.3	Submit journal article on the synthesis and application of acoustic MOF nanoparticles		6	6
	1.1.4	Develop additional polymer-coated MOF nanofluid candidates		8	8
1.2		*Stability Testing of Nanofluid Injectates*			
	1.2.1	Initiate nanofluid stability testing with MOF materials identified in sub task 1.1		1	1
	1.2.2	Measure surface charges of modified MOF nanoparticles and determine optimal nanofluid properties for transport in a sandstone.		3	3
	1.2.3	Submit journal article on the synthesis, stability, and geophysical signatures of a variety of MOF nanoparticles		9	9
1.3		*Seismic-frequency Experiments*			
	1.3.1	Complete impedance tube measurements of nanofluids and verify against core test experiments		1	1
	1.3.2	Complete elastic property measurements to enable calculations of seismic velocities, with results being transferred to subtask 1.5.		7	7
	1.3.3	Submit journal article detailing subtask 1.3 and 1.4 core-test results		12	12
	1.3.4	Initiate testing of final candidate nanofluids at expected subsurface, pressure, and temperature to evaluate nanofluid stability and acoustic response		5	5
	1.3.5	Initiate final series of FY22 core test measurements to enable calculations of seismic velocities, with results being transferred to Predictive Seismic Simulations		10	10
	1.3.6	Complete bringing LVDT core test online, including signals aquistion, processing, and analysis		8	8
1.4		*Ultrasonic Attenuation and Velocity Measurements*			
	1.4.1	Initiate ultrasonic measurements of acoustic attenuation at a range of pore pressures		1	1
	1.4.2	Identify minimum nanoparticle concentrations needed to co-optimize contrast agent performance and cost		2	2
1.5		*Predictive Seismic Simulations*			
	1.5.1	Finalize development of a mechanistic model for seismic waveform interactions with subwavelength acoustic metamaterials at multiple scales		2	2
	1.5.2	Conduct a surface-based seismic survey simulation parametrized by results from subtask 1.3 and 1.4		4	4
	1.5.3	Conduct a surface-based seismic survey simulation parametrized by continued results from core test experiments		11	11
1.6		*Field Test Development Plan*			
	1.6.1	Develop a site-specific field test plan that includes contrast agent type, concentration, cost, and injection strategy (SMART)	SMART	12	12