New Imaging and CO_2 Storage Technologies for Unconventional Subsurface Reservoirs

Task 1: Enhanced Contrast Agents for CO_2 Monitoring

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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

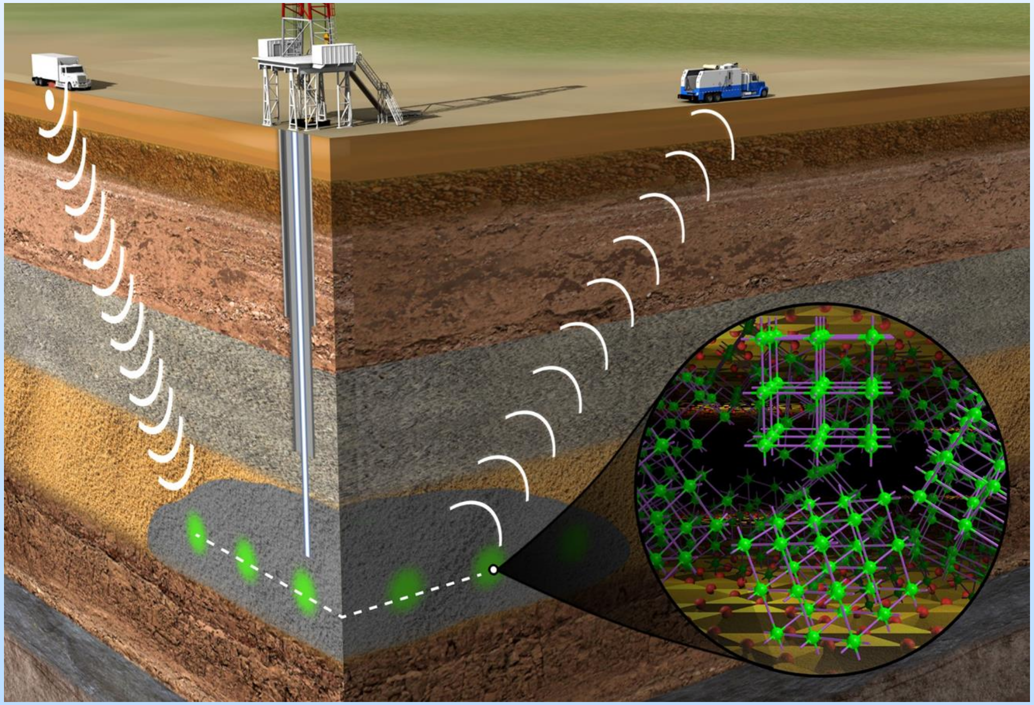
- Goal: Development of geologic storage technology with a near zero cost penalty goal – a grand challenge with enormous economic benefits.
- Objective: Employ a multidisciplinary approach for identifying key sequestration opportunities and for pursuing major research needs in for development of acoustically 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 colloidal nanoparticle suspensions (nanofluids)
- Detection through conventional seismic imaging

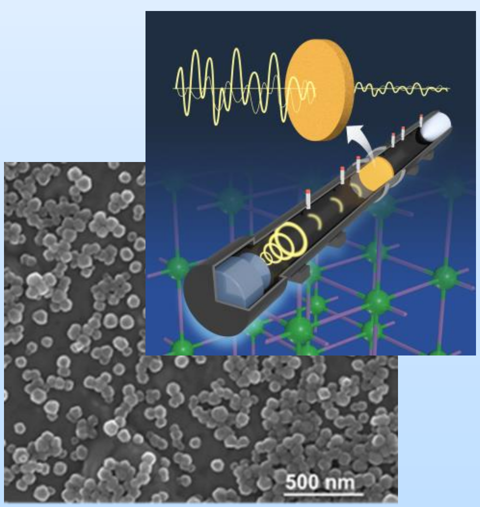
Goal: Develop contrast agents for time-resolved monitoring/mapping of subsurface fluids and fracture networks

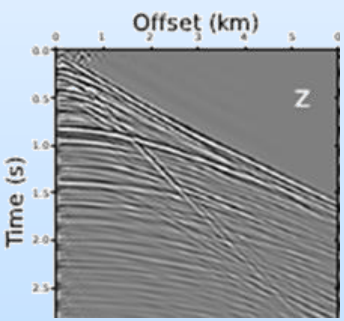


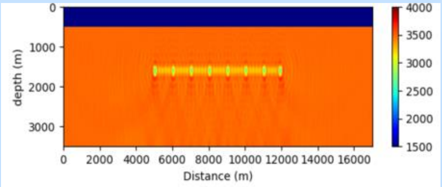
Project Overview

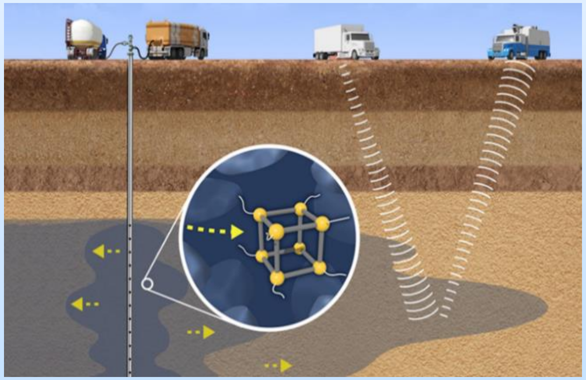
- Task 1 – Enhanced Monitoring Agents
  - 1.1-1.2 Synthesis and Stability Testing
  - 1.3-1.4 Laboratory-Based Core Test Experiments
  - 1.5 Predictive Seismic Simulations
  - 1.6 Field Test Plan Development

Synthesis ⟷ Experiments ⟷ Simulations ⟷ Field Test Plan







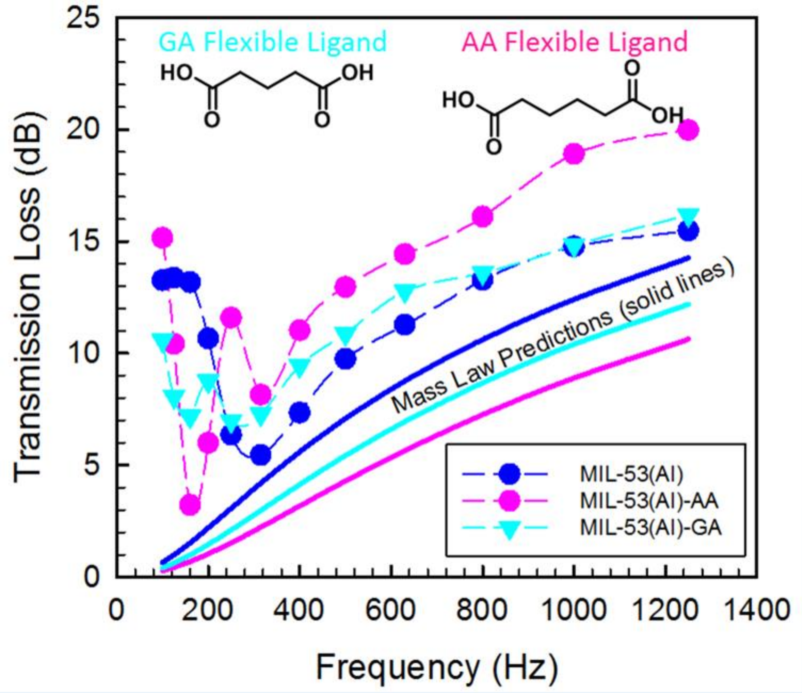


Molecular › Micro › Bench › Systems › Deployment › Vision

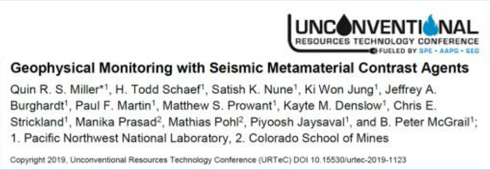
MOFs are Acoustic Metamaterials that Influence Elastic/Anelastic Properties of Rocks

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



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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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Injectable Contrast Agents for Enhanced Subsurface Mapping and Monitoring

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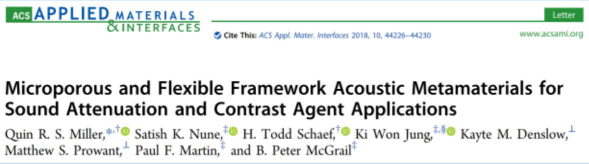

ACS APPLIED MATERIALS & INTERFACES

Letter

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

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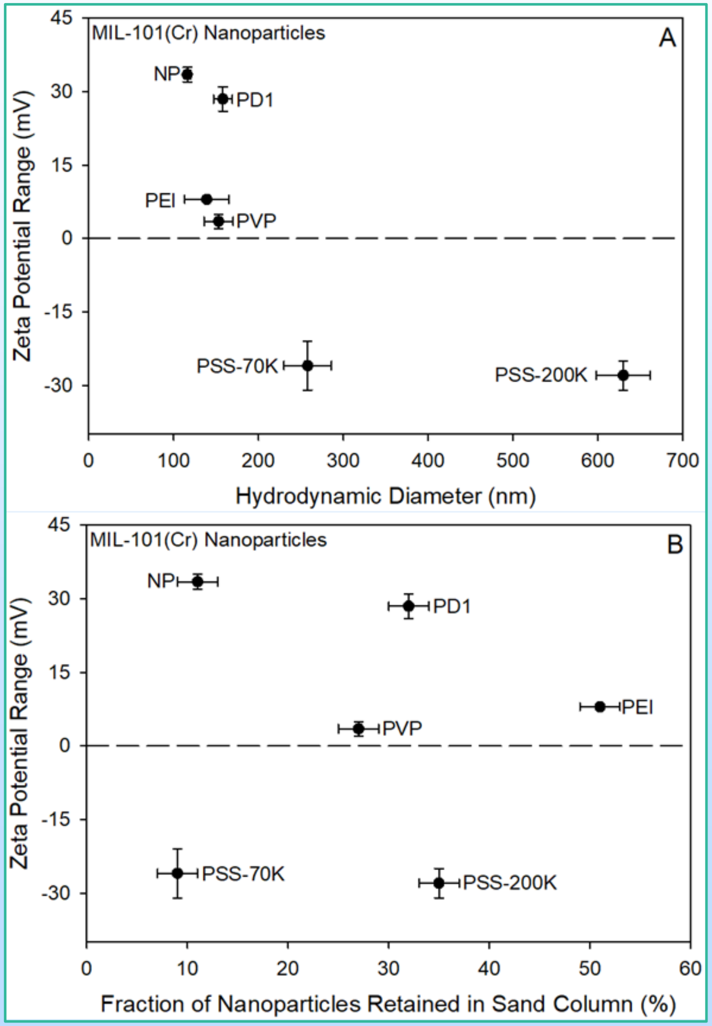
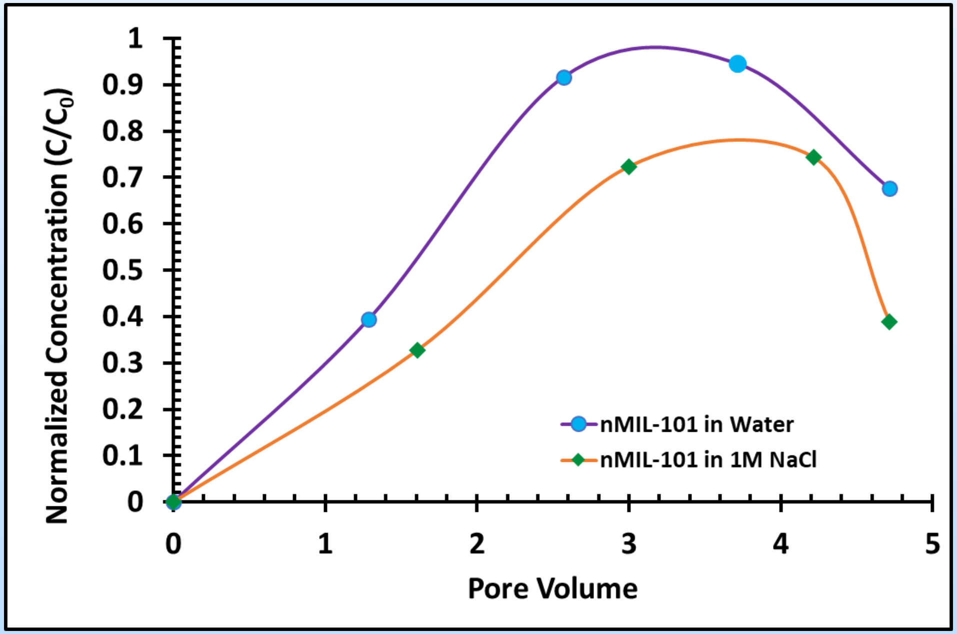
Polymer Coatings Increase Colloidal Stability

Column experiments with silica sand (negative surface charges) used to evaluate nanoparticle transport/retention and the influence of polymer coatings.



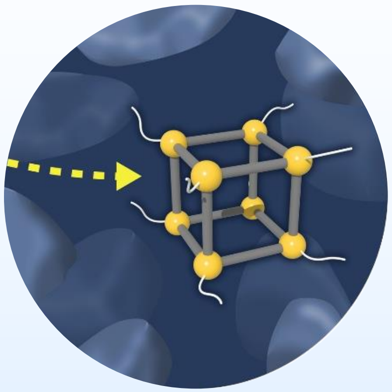
Down-selection of polymer coatings:

- 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
- Additional stability/transport testing with up to 3M NaCl solution are ongoing

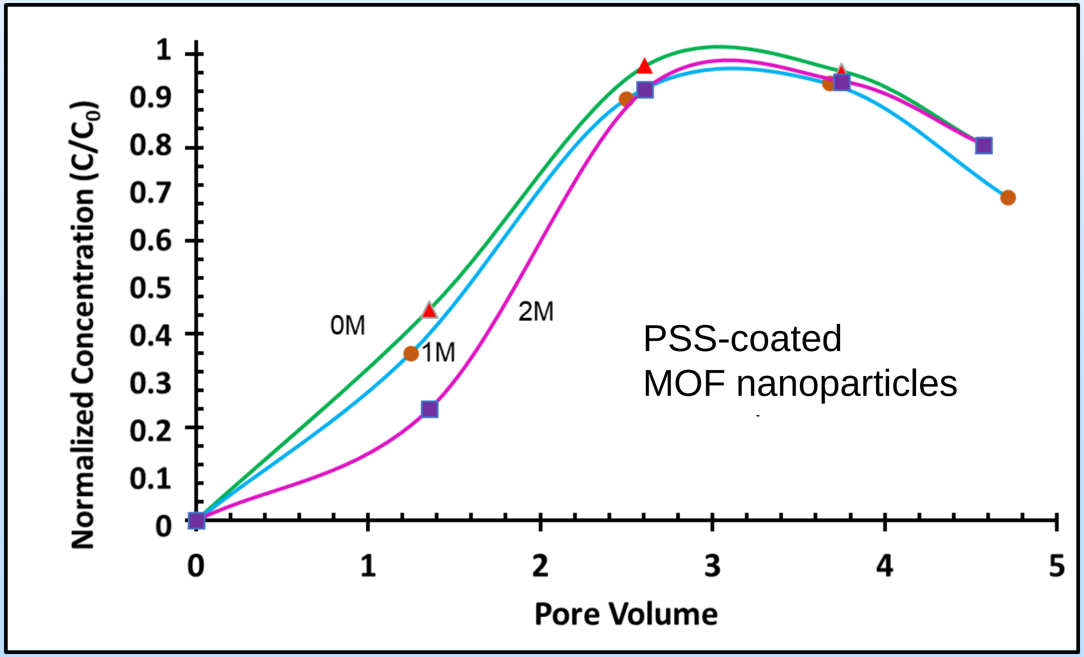


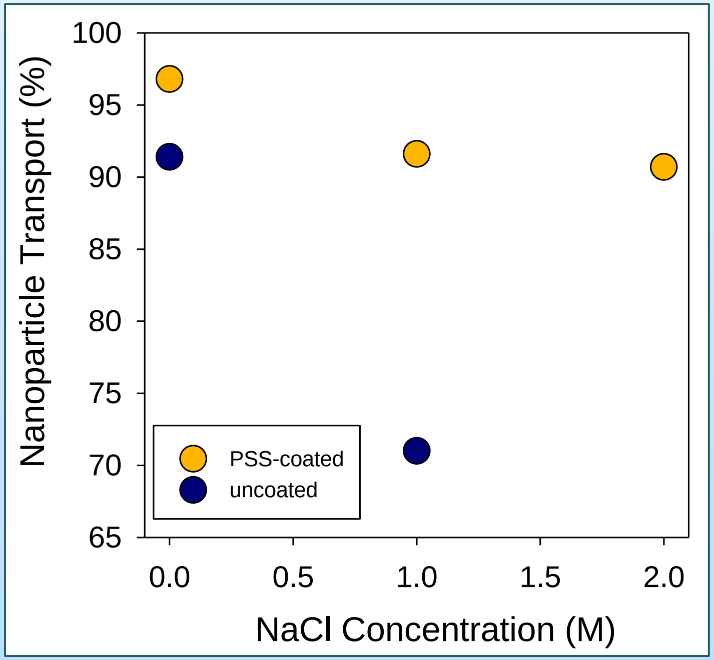
9% (water) vs 29% (1M NaCl) uncoated nanoparticle retention

Polymer Coatings Enhance Transport in Porous Media



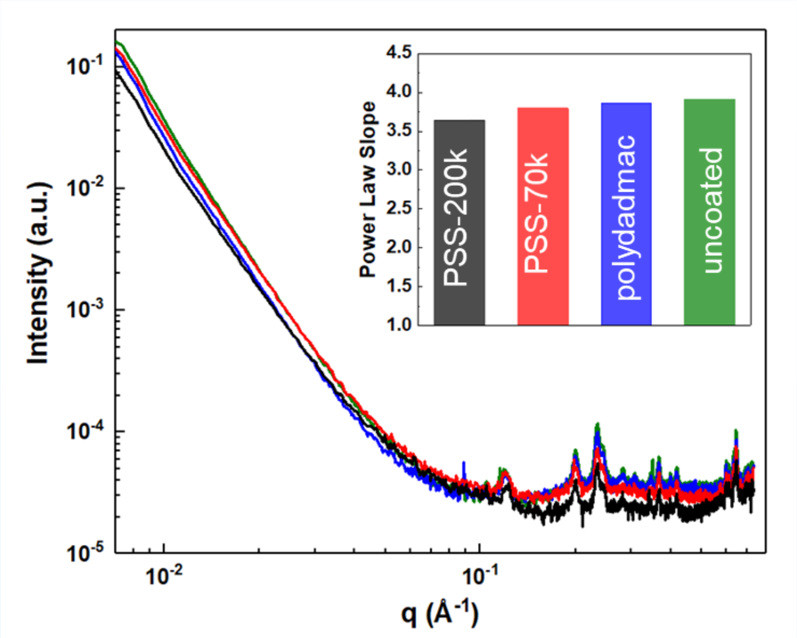
- Polymer (PSS) coatings reduced retention of nanoparticles in the column experiments at 1-2M NaCl relative to DI water conditions
- Breakthrough curves for MOF nanoparticle transport are similar due to PSS coatings
- Only small decreases observed in nanoparticle transport with increasing ionic strength
- Repulsion from silica surfaces and other nanoparticles promotes efficient transport

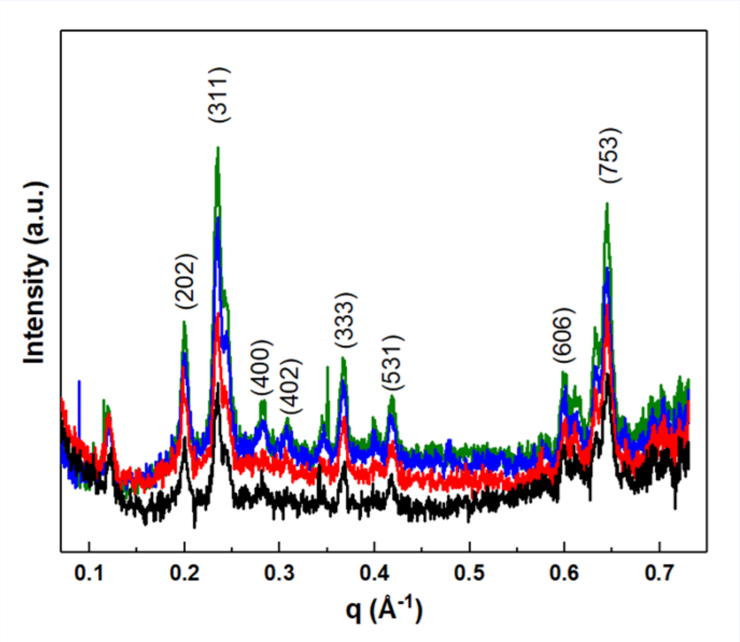




Small-Angle X-Ray Scattering (SAXS) Provides Insight into Polymer-Coated Nanofluid Structure and Stability: Preliminary Results

- SAXS provides information on structure, particle size distributions, spatial arrangements of particles, surface features, and pore network architecture
- SAXS confirms polymer coatings don't impede the formation of stable MOF nanoparticles
- Decreasing trend in power law slopes indicate transformation towards mass fractals from surface fractals, helping us decipher the surface properties that lead to retention/transport

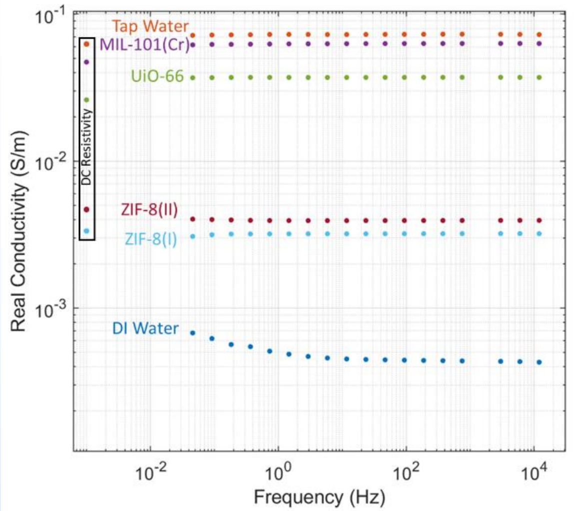


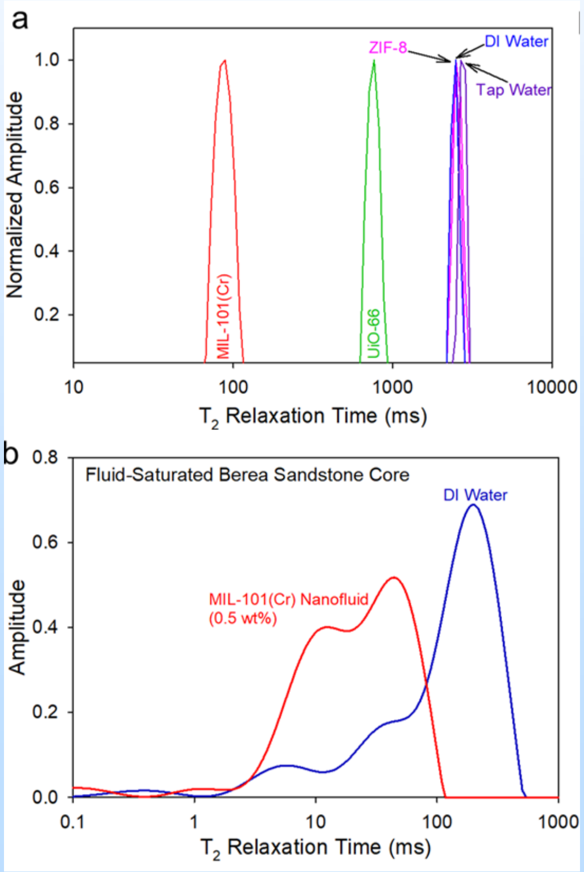


- Next: Influence of ionic strength on nanofluid Å- to µm-scale structure, we will probe a larger range of fluid conditions and length scales

Acoustic Nanoparticles are Multimodal Contrast Agents: NMR and Electrical Signatures

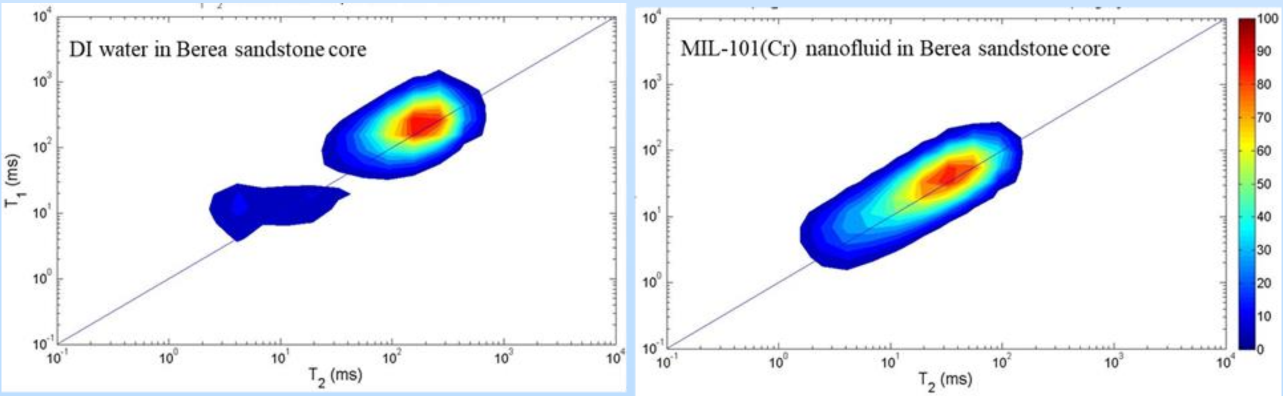
- Nanofluids have distinct conductivity/resistivity signatures
- Nuclear Magnetic Resonance (NMR) response related to framework hydrophilicity and presence of paramagnetic cation





In Situ NMR for MOF in Berea Sandstone

- 2D maps of T1-T2 relaxation times, indicative of how protons in the pore fluid H2O are relaxing in the longitudinal (T1) and axial (T2) planes, used to distinguish fluid types
- Preservation of T1-T2 ratio allows for identification of fluid type in multicomponent systems where MOFs may be used to determine mobile fluid fractions.

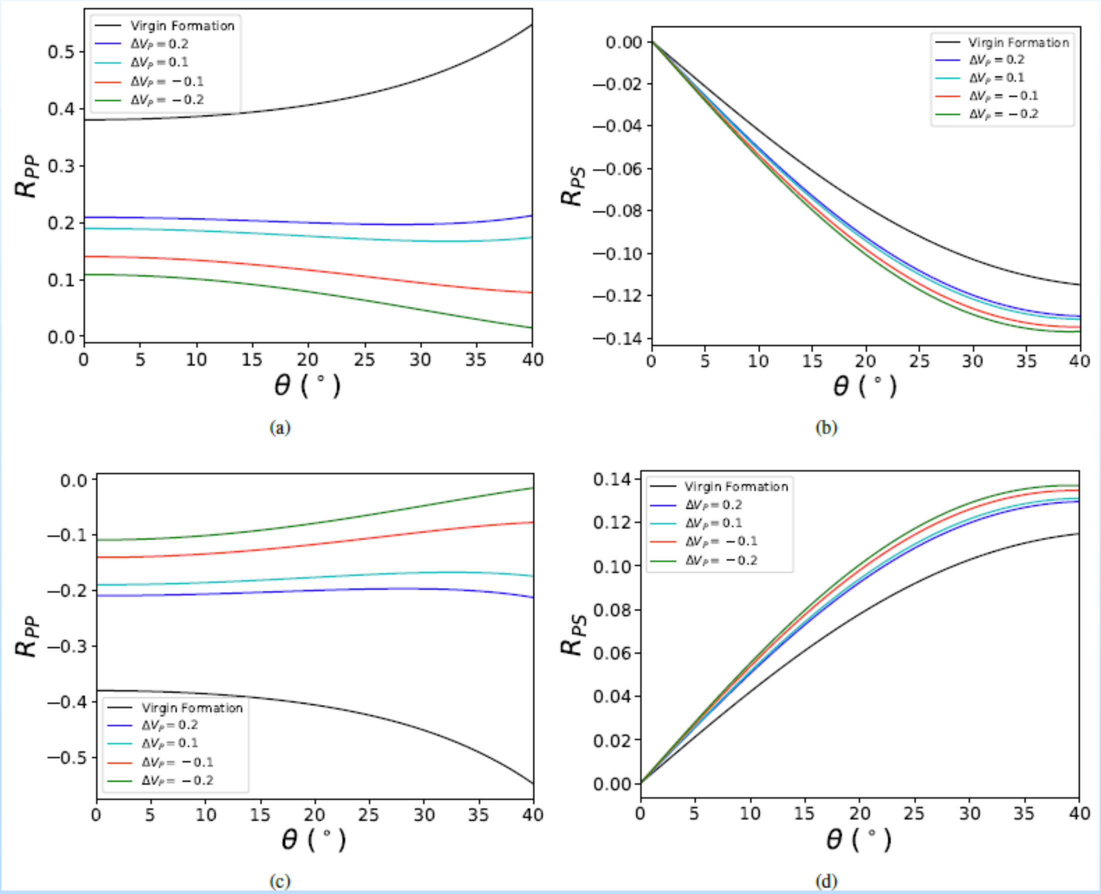


Amplitude Variation with Angle (AVA) Seismic Simulations

- 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 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.

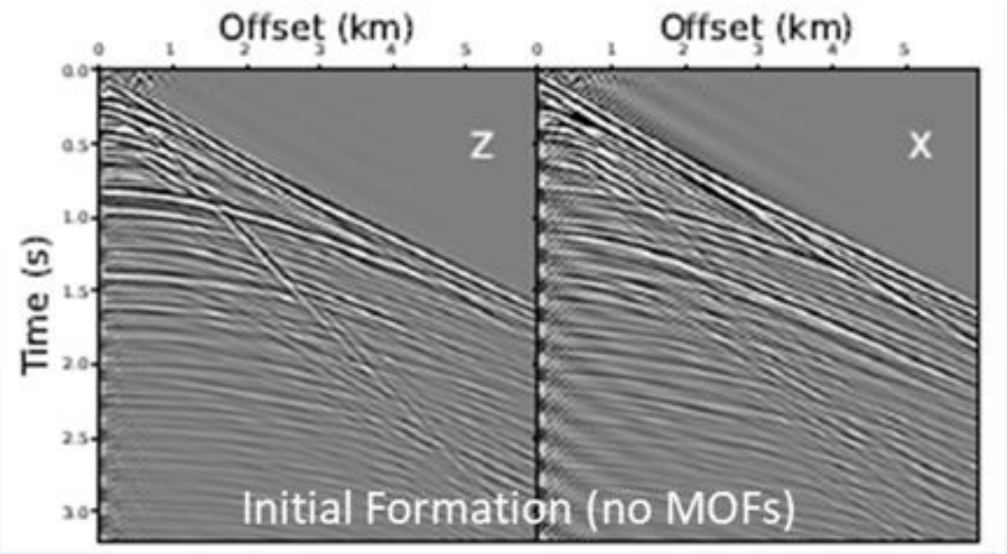
AVA parameters can be robustly extracted from seismic data, PP-wave AVA analysis will be extremely useful in the spatio-temporal imaging of MOFs in the subsurface.

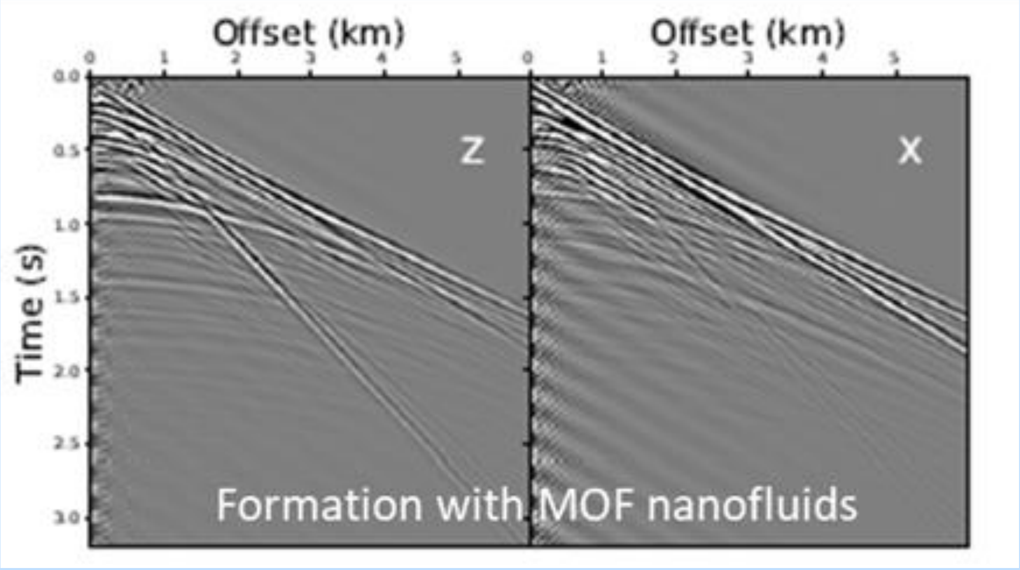


Full Wavefield Modeling Seismic Simulations

- The modeled seismograms are composed of vertical and horizontal wavefield components
  - Z is perpendicular (vertical) to the earth's surface
  - X is parallel (horizontal) to the earth's surface.
- Full wavefield elastic wave modeling for three different levels of attenuation
- With increasing MOF concentration, the reflections from below the sandstone layer get significantly attenuated.

These amplitude losses will be clear in seismic data and are valuable signals of contrast agent location in the reservoir.





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
- Successful ongoing collaborations with research groups of Prof. Manika Prasad’s (CSM) and Prof. Greeshma Gadikota (Cornell)
- Results presented at AGU, ACS, and AIChE

Acknowledgements

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Jeff Burghardt, Michael Sinnwell, Paul Martin

Manika Prasad, Mathias Pohl, Jyoti Behura, Kurt Livo

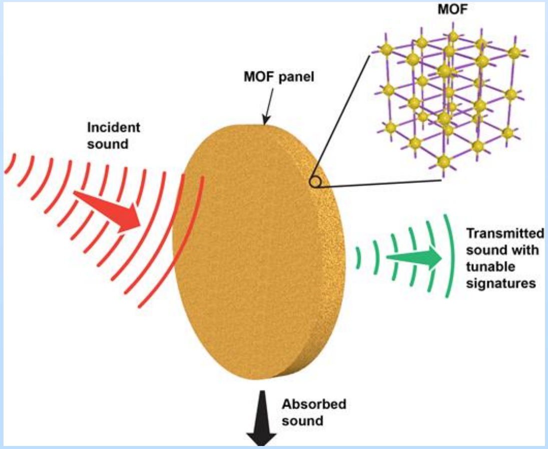
Greeshma Gadikota, Hassnain Asgar

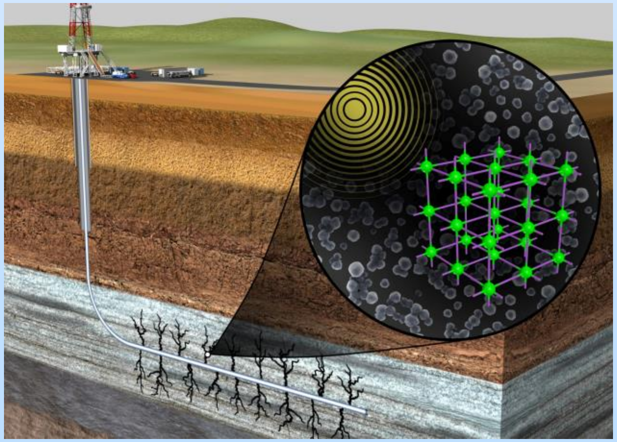
Relevant Publications

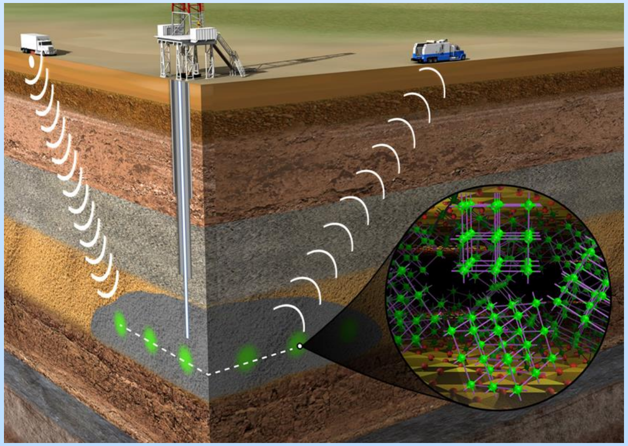
- Miller, Q.R.S., H.T. Schaef, S.K. Nune, K.W. Jung, J.A. Burghardt, P.F. Martin, M.S. Prowant, K.M. Denslow, C.E. Strickland, M. Prasad, M. Pohl, P. Jaysaval, B.P. McGrail. **(2019)** "Geophysical Monitoring with Seismic Metamaterial Contrast Agents". Unconventional Resources Technology Conference (URTeC) Proceedings., 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

2020 In Preparation

- Nune et al., "Transport of polymer-coated metal-organic framework nanoparticles in porous media"
- Miller et al., "Metal-organic framework colloidal nanoparticles as injectable multimodal contrast agents for subsurface sensing"







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 Physical & Computational Sciences Directorates at PNNL
- Pacific Northwest National Laboratory is Operated by Battelle Memorial Institute for the Department of Energy

Gantt Chart

Task	Milestone	Title	G/N	Begin	End	FY20 Q1 1	FY20 Q2 2	FY20 Q3 3	FY20 Q4 4	FY21 Q1 1	FY21 Q2 2	FY21 Q3 3	FY21 Q4 4
1.0		**Enhanced Contrast Agents for CO2 Monitoring**		0	5								
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		4	4				▲				
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			▲					
1.3		*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.		5	5					▲			
	1.3.3	Submit journal article detailing subtask 1.3 and 1.4 core-test results		5	5					▲			
	1.3.4	Initiate testing of final candidate nanofluids at expected subsurface, pressure, and temperature to evaluate nanofluid stability and acoustic response		4	4				▲				
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				▲				
1.6		*Field Test Development Plan*											
	1.6.1	Develop a field test plan that includes contrast agent type, concentration, cost, and injection strategy (SMART)	SMART	5	5					◆			