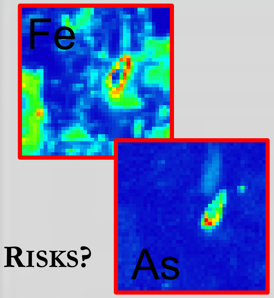
In-Situ Groundwater Monitoring

Understand natural Background variability



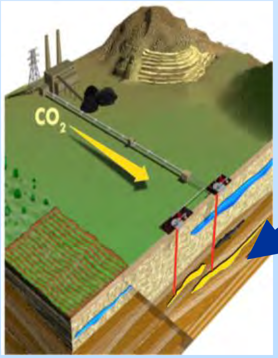
Risks?

Lab Methods – complex waters

Continuous CO_2 Monitoring Devices

PA Karst Springs (Natural Analog)

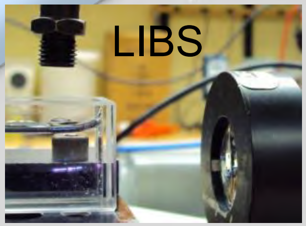
- Develop & demonstrate a suite of geochemically-based in-situ monitoring strategies for groundwater systems
- Determine sensitivities of techniques in real world conditions



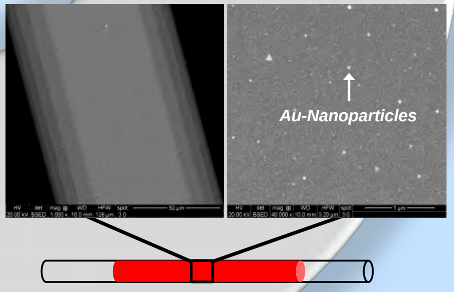
Migration into Shallow Aquifers

Migration into other Deep Formations

Validate/ensure 99% storage permanence



FO Coatings



Test and validate the use of CO_2 monitoring devices under field conditions

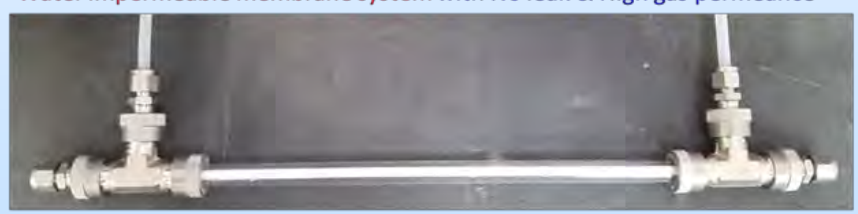
In-Situ Geochemical Monitoring

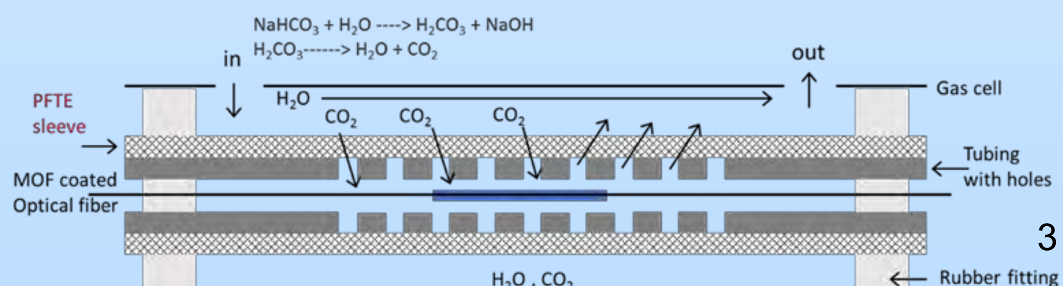
- **Task 22:** Direct CO_2 Sensing in Groundwater
  - deliver a inexpensive, continuous, downhole NDIR, telemetry-based sensing method for the real-time detection of dissolved CO_2 concentrations in groundwater that are indicative of leaks from geological storage sites.
- **Task 23:** Distributed Fiber Optic Based CO_2 Sensors for Carbon Storage Applications
  - deliver a viable CO_2 sensing technology, that can monitor CO_2 in geological formations relevant for CCS applications. Demonstrate CO_2 sensor with a sensitive (< 1 percent) and selective/stable response in the presence of water
- **Task 24:** Laser Induced Breakdown Spectroscopy (LIBS)
  - deliver a LIBS flow through apparatus capable of measurements of subsurface fluids in contact with real and manmade materials under in situ conditions. This work will deliver a laboratory based experimental apparatus that can withstand elevated temperature and pressure which can be used alongside the field deployable LIBS instrument that is currently being tested

Challenges to Current Practices

- **Laboratory-based analyses can be time consuming, have significant lag-time between sampling and analysis, and may be impractical for real-time monitoring of leaks**
- **Even field deployments of existing sensing commercial technologies require advances in packaging and methodology**
- **This work improves on the current practices:**
  - Advancing the science-base for potential novel in-situ analysis techniques

Water impermeable membrane system with No leak & High gas permeance





Geochemical Monitoring:
Direct Sensing: CO_2 in Shallow GW

- Non-Dispersive Infrared (NDIR)



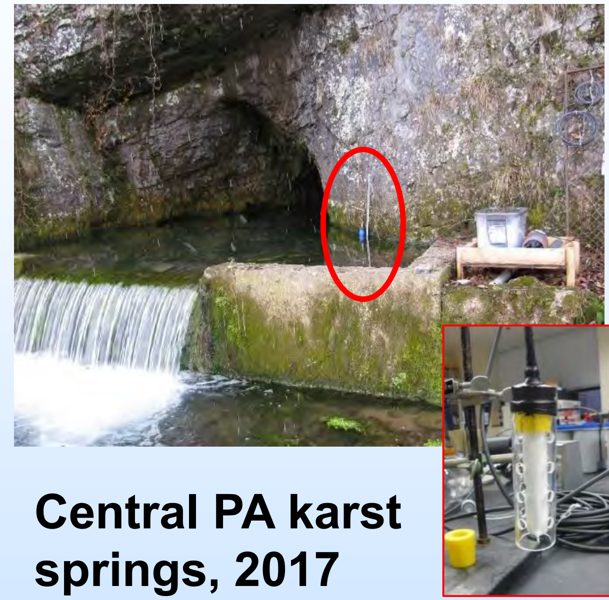

- Adapted from atmospheric sensors (Vaisala)
- < 1 mg/L lower limit
- NETL-adapted to sample pumped water
- Sensor modified for field deployment
- Commercial marine sensor being tested

PI - Edenborn

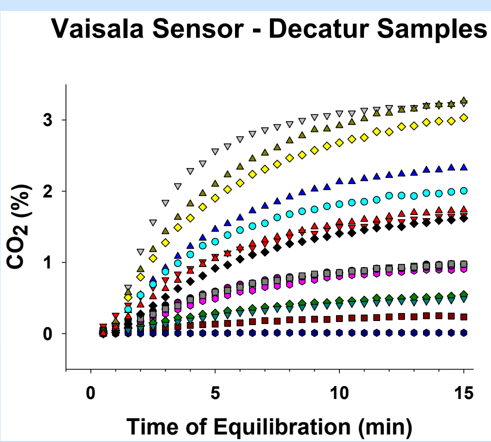
Geochemical Monitoring:
Field Testing and Validation

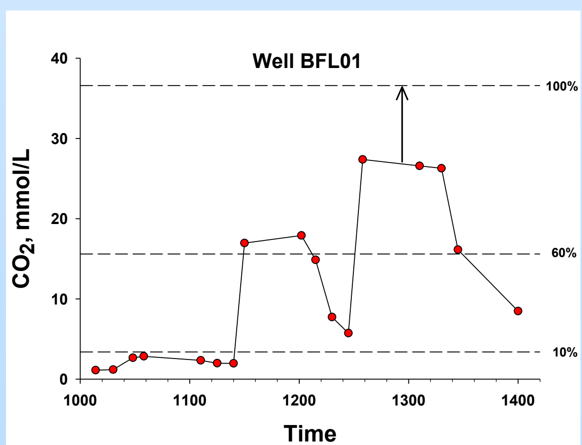
Decatur IL ADM Plant, 2015-16

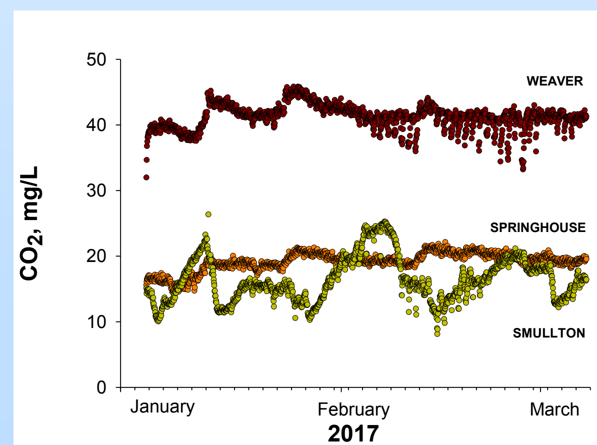
Brackenridge Field Site, Austin, TX 2016-2017



Central PA karst springs, 2017





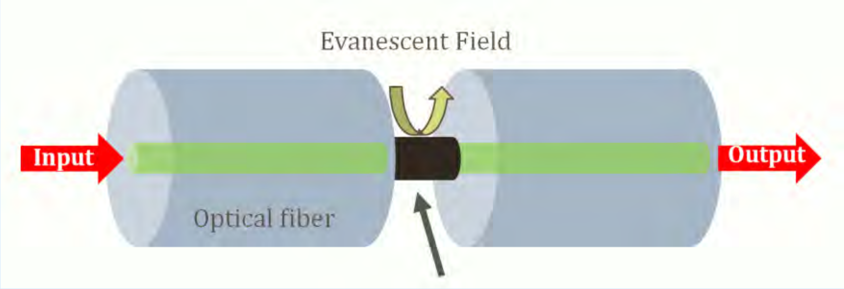


Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

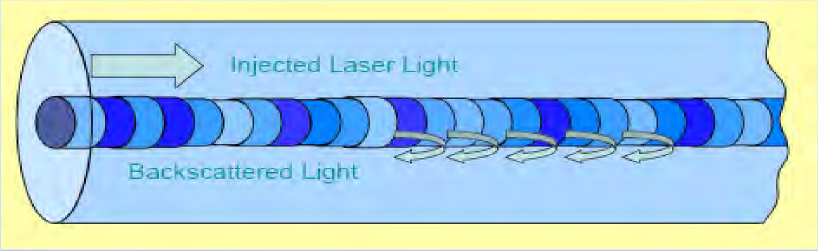
NETL RIC Optical Fiber Sensor Efforts are Targeted at Distributed Chemical Sensing for Environmental Monitoring

Leverage In-House Capabilities in ***Functional Materials***, ***Optical Sensing*** and ***Geochemistry***

Nanomaterial Enabled Chemical Sensing



Nanomaterial Sensing Layer



Compatible with Distributed Interrogation

- Engineered nanomaterials for chemical sensing parameters of interest
- Versatile and can be applied to any environmental parameters of interest
- Distributed interrogation permits "mapping" along the length of the fiber
- Examples: pH, CO_2, and CH_4
- Current project focuses directly on CO_2

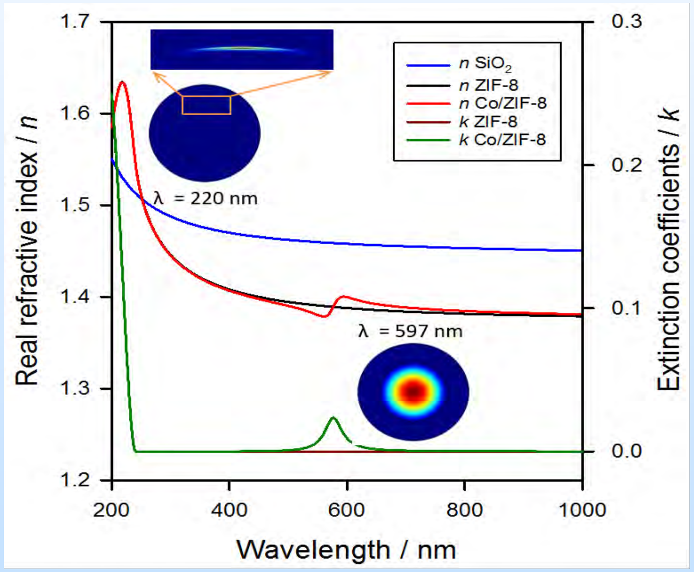
Products in 2018: 2 patents awarded, 2 peer-reviewed manuscripts published

PI - Ohodnicki

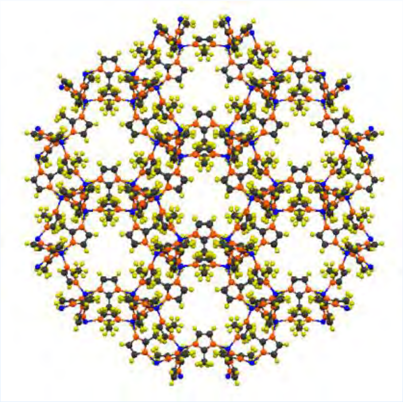
Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

Evanescent Wave Absorption Based Sensors

$$I_T(\lambda) = I_0 \exp[-\gamma\alpha(\lambda)CL]$$



Metal organic framework (MOF)

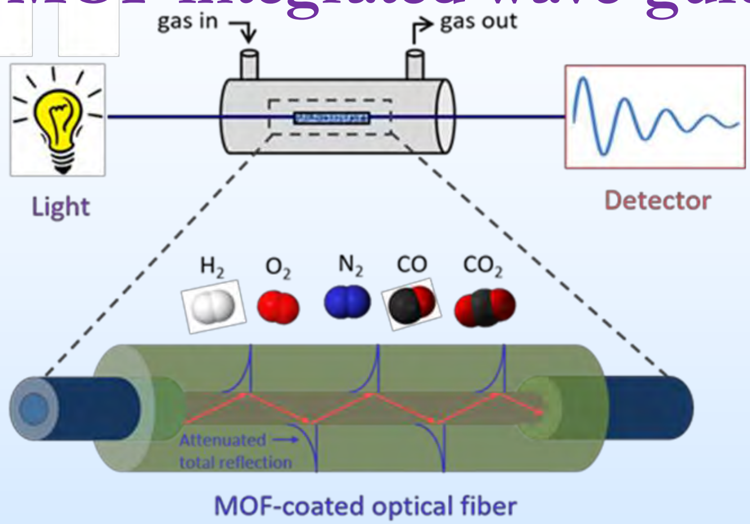


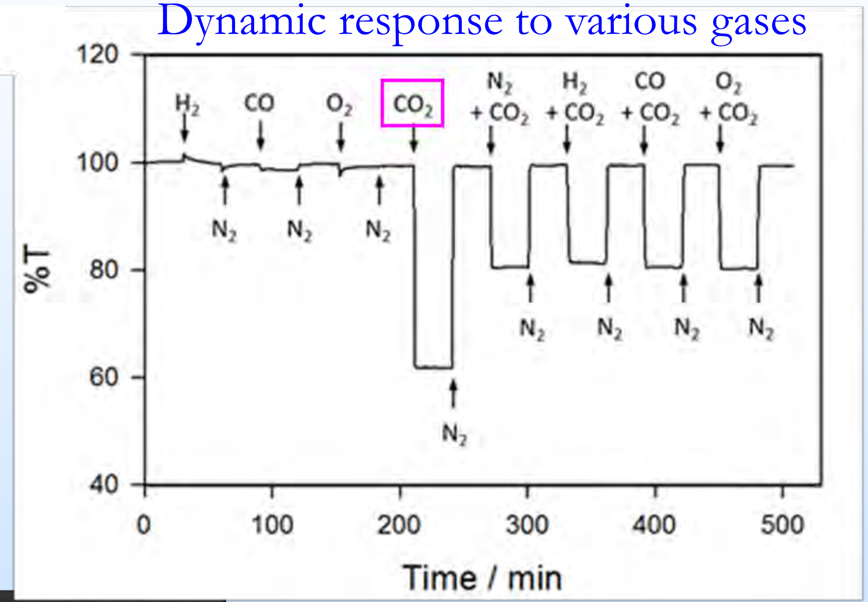
Polymers

An emphasis is being placed on metal-organic framework materials but recent efforts are also considering polymers as well.

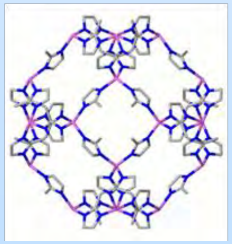
Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

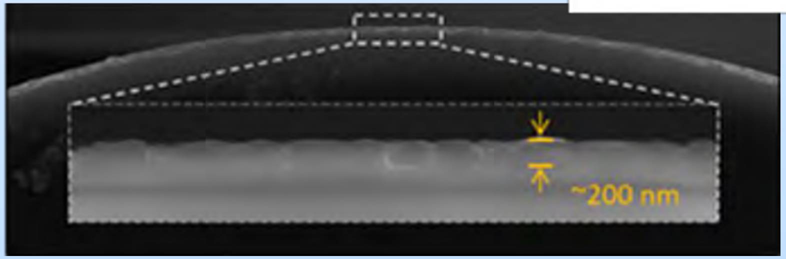
- **MOF integrated wave-guide CO_2 gas sensor**





ZIF-8 MOF

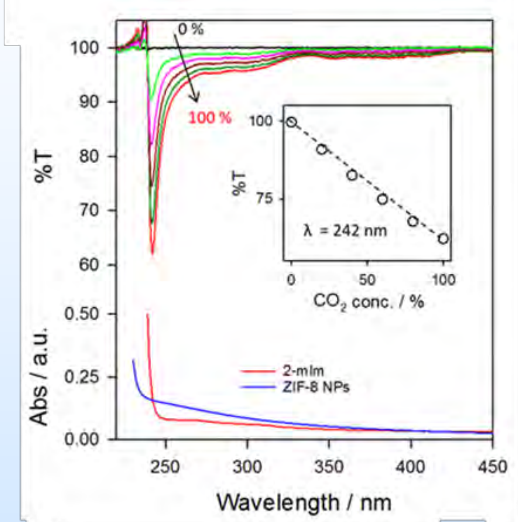


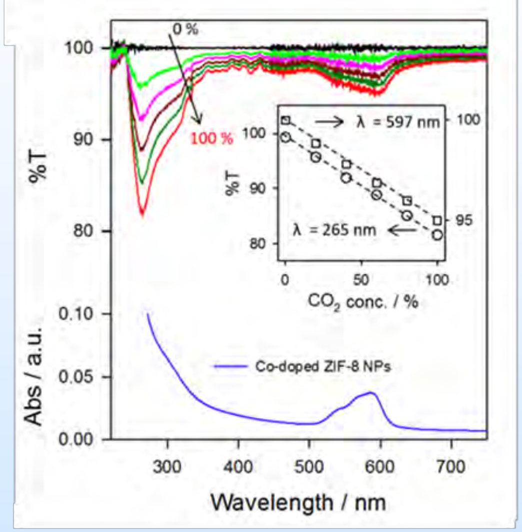


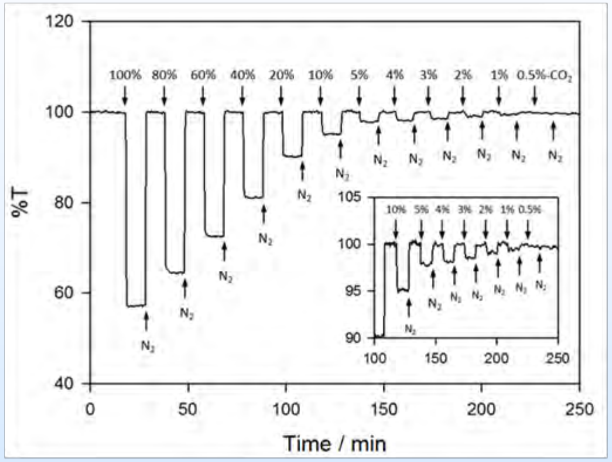
Highly selective, sensitive films have been developed and demonstrated for CO_2 sensing in gas phase environments leveraging metal-organic framework materials.

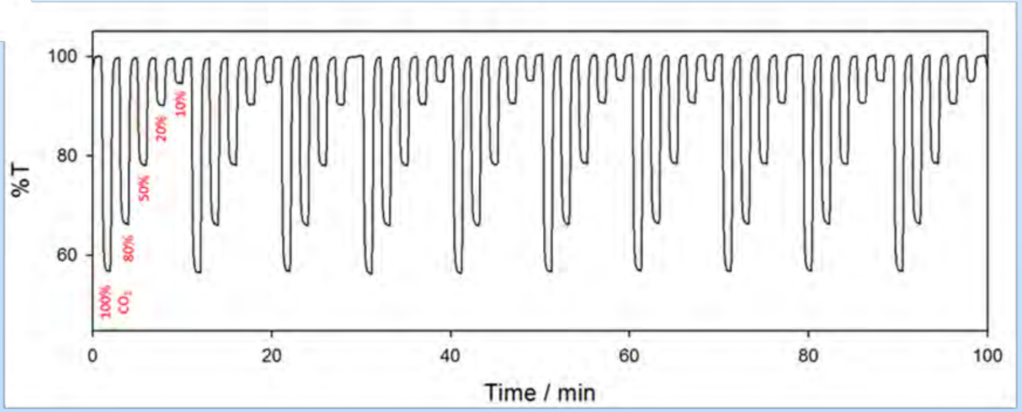
Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

- MOF integrated wave-guide CO_2 gas sensor









- Great promise for gas sensing of CO_2.
- Excellent selectivity to CO_2.
- Very fast (< 1 minute) response times and excellent reversibility.
- Improved scientific understanding of sensing mechanism for the optical fiber platform.

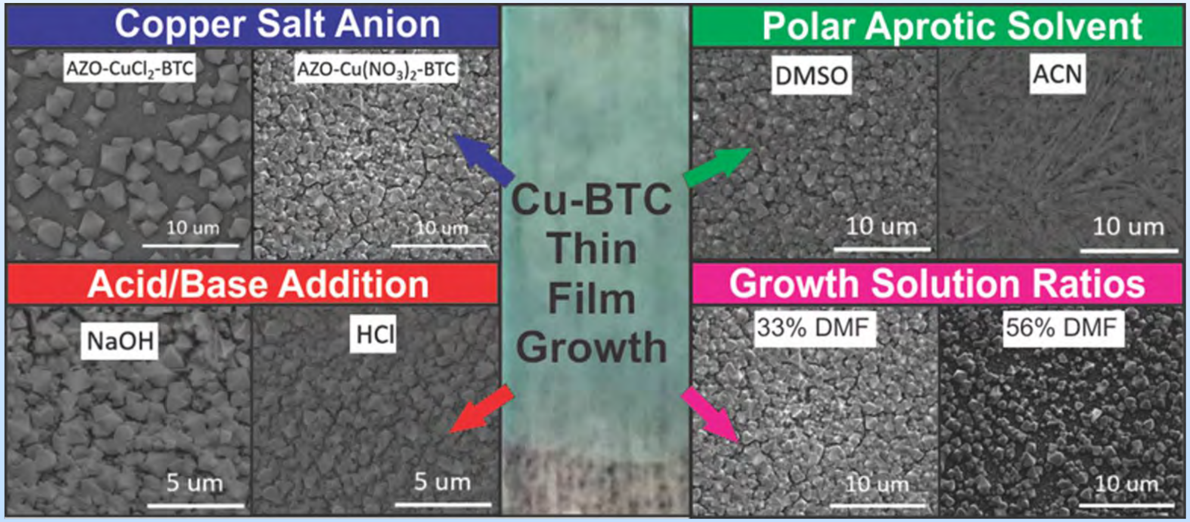
ACS Sensors, 2018, 3, 386-394.

Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

- **Rapid, selective and room temperature growth of MOF thin films on conductive metal oxide for CO_2 gas sensors**

Template | Conductive metal oxide layer on template | Hydroxy double salt layer on template | MOF layer on template

Cryst. Growth Des., 2018, 18, 2924-2931.

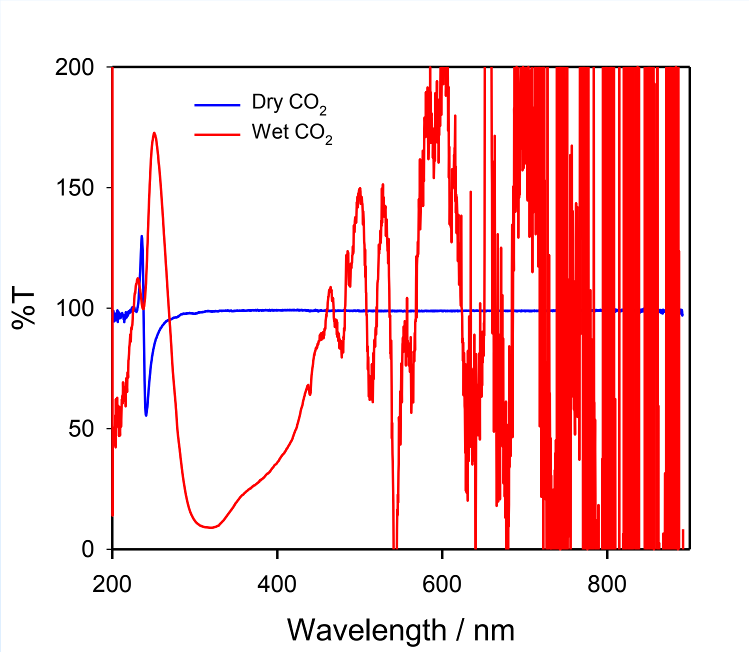


New growth techniques are being explored and developed for long-length fiber optic sensors compatible with distributed interrogation methods.

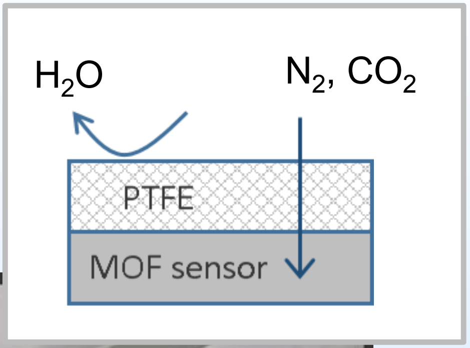
Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

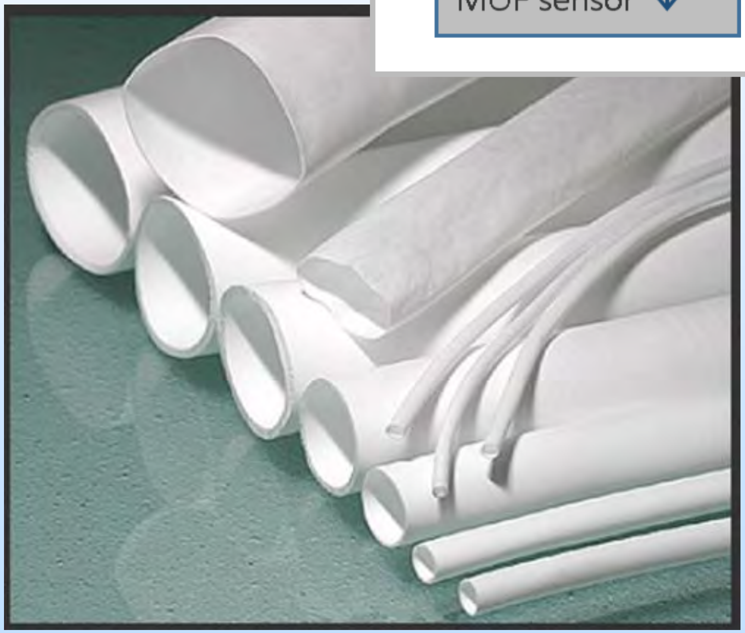
- **MOF integrated wave-guide CO_2 gas sensor**
- **Water vapor impacts**

Without modifications to engineered sensing layers, water vapor has significant impacts on the response.



Air permeable but water impermeable **PTFE sleeve.**

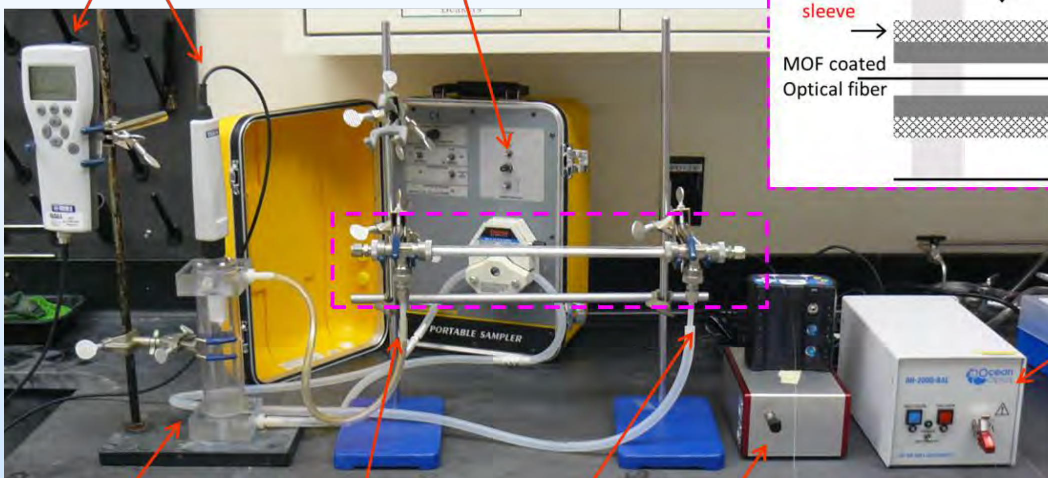




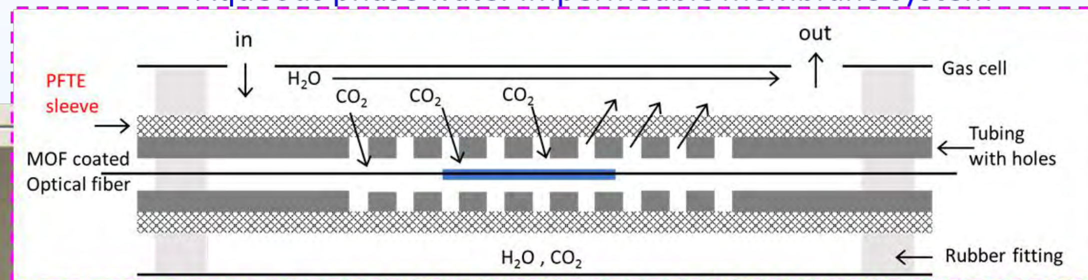
Water vapor impacts are being explored and techniques / learnings from field deployments underway for commercial technologies are being applied.

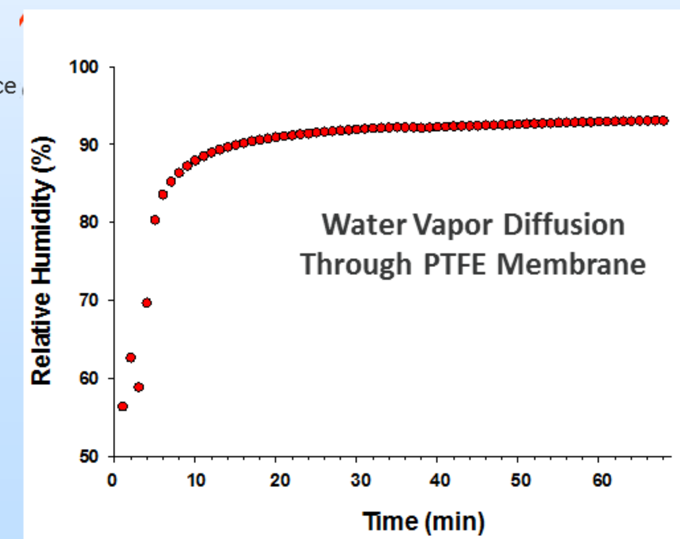
Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

- Test facility at the NETL "field testing" laboratory



Aqueous phase water impermeable membrane system



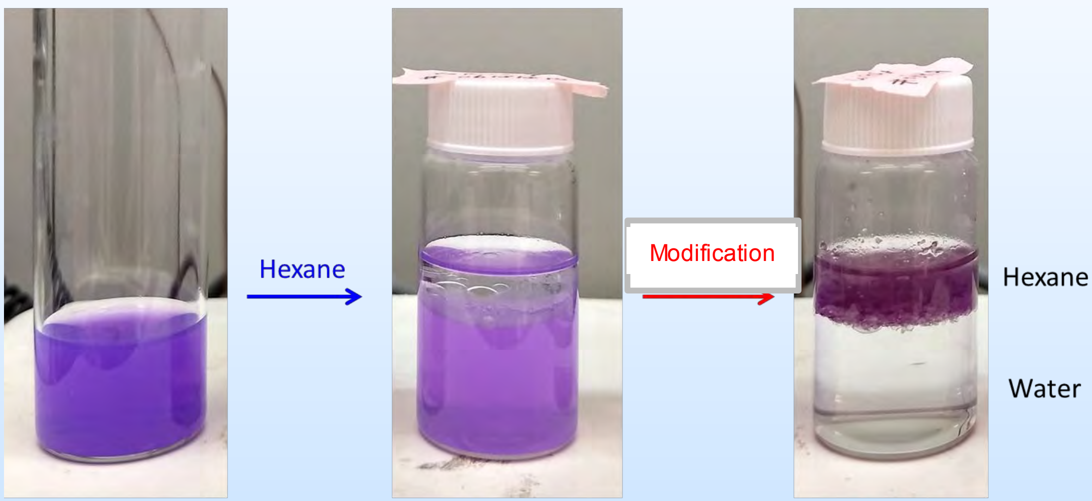


The NDIR sensor being field tested can be applied "in-line" to prepare for future field testing efforts.

A new lab facility has been established to simulate groundwater with varying CO_2.

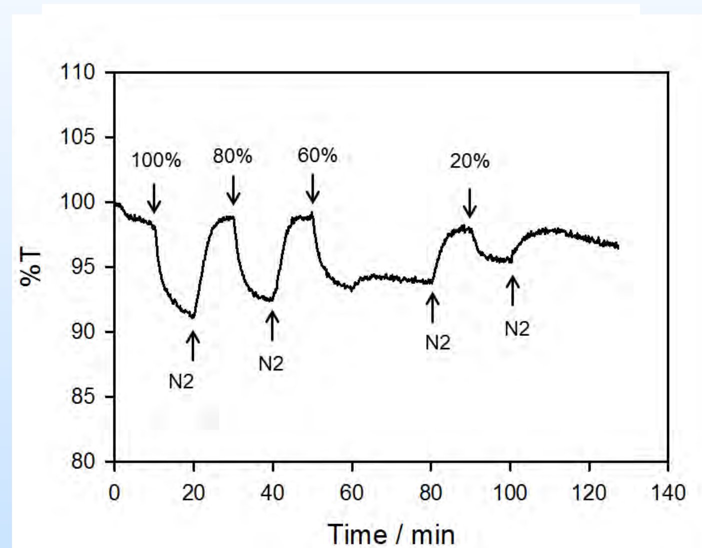
Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

➢ **Surface modification of MOF**



Pristine MOF **Modified MOF**

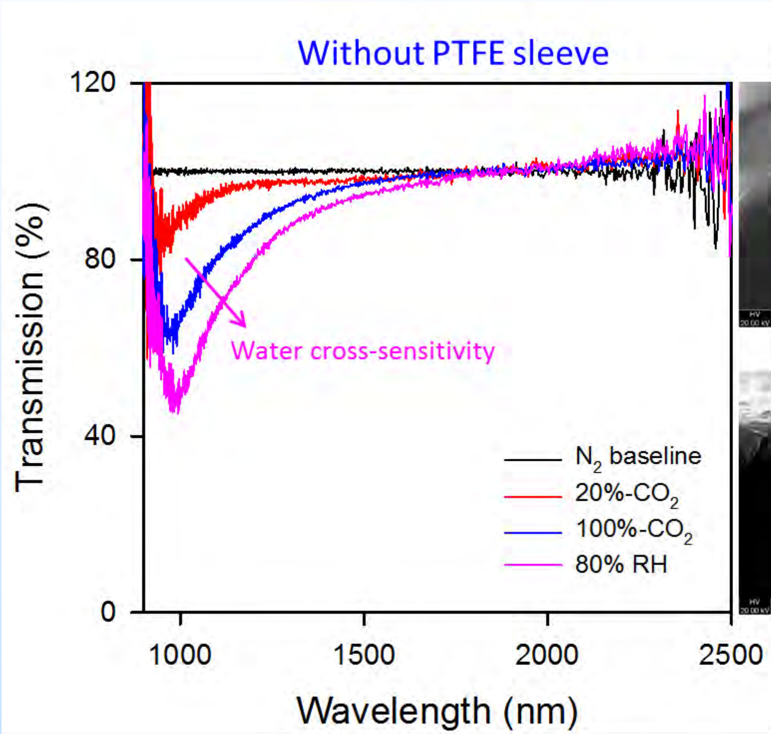
CO_2 sensing results for a modified MOF in the presence of 80% relative humidity

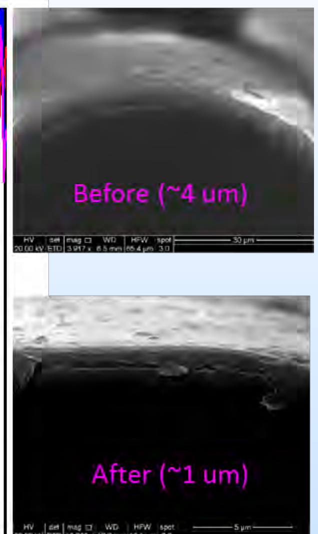


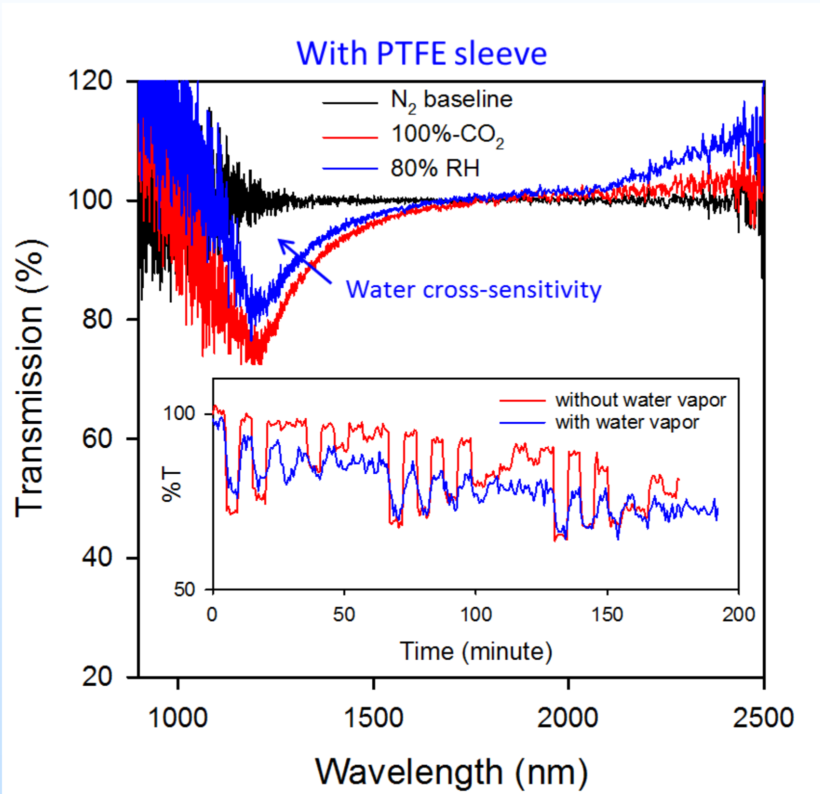
Surface modifications to existing sensing layers are being explored to develop hydrophobic behavior, preliminary results show enhanced CO_2 sensing with water vapor.

Geochemical Monitoring:
Nanomaterial Enabled Fiber Optic Chemical Sensors

➢ **Engineered hydrophobic polymers for CO_2 sensing**

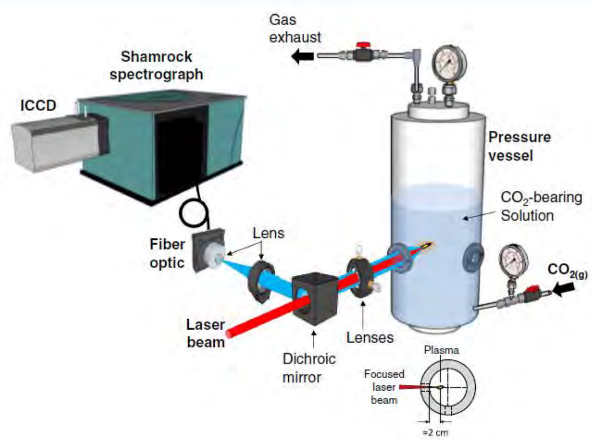


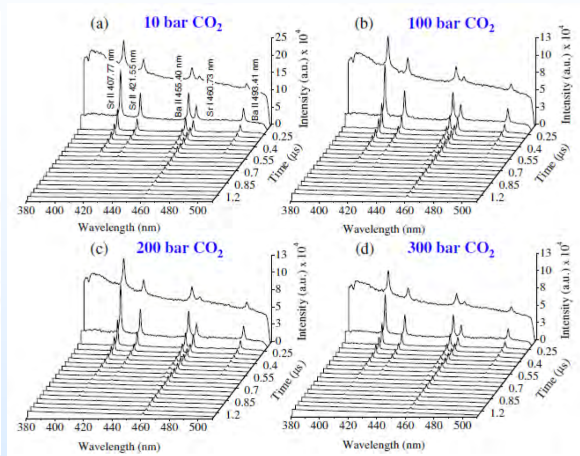




- ❑ **PTFE sleeves help to mitigate water vapor cross-sensitivity and enable reversible sensing of CO_2**
- ❑ **Modifications to the engineered polymer based films are observed after water vapor exposure**
- ❑ **Sensing materials that selectively absorb CO_2 gas and mitigate water vapor are being developed**

Geochemical Monitoring:
Laser Induced Breakdown Spectroscopy (LIBS)





- Measurement of multicomponent system
  - Chloride Solutions of Ba, Ca, Mg, Mn, Sr
  - Limits of Detection and Quantification vs. Pressure
  - Emission decay vs. pressure vs. element
- Laboratory experiments successfully demonstrate that low-ppm range concentrations of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Mn^{2+} can be accurately measured in CO_2-laden water at varied pressure conditions by using underwater LIBS.

Metal ions	S	R^2	LOD (ppm)	LOQ (ppm)	CO_2 (bar)
Mg^{2+}	$0.0019 \pm 2.93 \cdot 10^{-5}$	0.9993	31.68 ± 0.92	104.53 ± 1.06	10
	$0.0023 \pm 3.56 \cdot 10^{-5}$	0.9996	31.12 ± 0.78	102.71 ± 2.54	200
	$0.0022 \pm 1.87 \cdot 10^{-5}$	0.9998	30.83 ± 1.05	101.73 ± 3.74	400
Ca^{2+}	$0.0114 \pm 1.16 \cdot 10^{-4}$	0.9996	2.48 ± 0.71	8.18 ± 0.20	10
	$0.0118 \pm 3.85 \cdot 10^{-4}$	0.9958	2.45 ± 0.62	8.09 ± 0.09	200
	$0.0111 \pm 2.46 \cdot 10^{-4}$	0.9980	2.67 ± 0.30	8.81 ± 1.01	400
Sr^{2+}	$0.0076 \pm 6.83 \cdot 10^{-5}$	0.9998	3.34 ± 0.11	11.02 ± 0.97	10
	$0.0080 \pm 3.07 \cdot 10^{-4}$	0.9956	3.04 ± 0.13	10.04 ± 1.34	200
	$0.0080 \pm 1.37 \cdot 10^{-4}$	0.9991	3.38 ± 0.31	11.15 ± 1.02	400
Ba^{2+}	$0.0037 \pm 3.53 \cdot 10^{-5}$	0.9997	4.38 ± 0.21	14.42 ± 2.03	10
	$0.0038 \pm 2.13 \cdot 10^{-5}$	0.9998	4.86 ± 0.12	16.05 ± 1.09	200
	$0.0036 \pm 5.06 \cdot 10^{-5}$	0.9994	3.91 ± 0.45	12.91 ± 3.23	400
Mn^{2+}	$0.0050 \pm 7.94 \cdot 10^{-5}$	0.9989	10.47 ± 0.13	34.53 ± 1.05	10
	$0.0062 \pm 1.76 \cdot 10^{-4}$	0.9968	7.42 ± 0.09	24.50 ± 1.00	200
	$0.0064 \pm 1.06 \cdot 10^{-4}$	0.9989	5.24 ± 0.05	17.27 ± 0.55	400

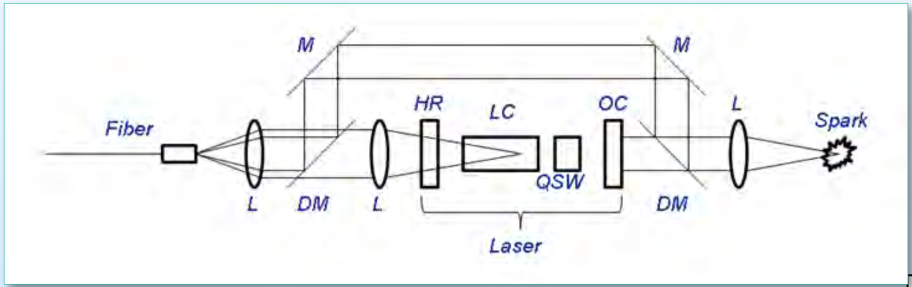
Goueguel, C.L. et al "Quantitative determination of metal ions in high-pressure CO2-water solutions by underwater laser-induced breakdown spectroscopy" in prep

PI - McIntyre

Geochemical Monitoring:
Laser Induced Breakdown Spectroscopy (LIBS)

Miniaturized Probe Development

- **Method and Device or Remotely Monitoring An Area Using a low Peak Power Optical Pump, US Patent 8786840 B1**



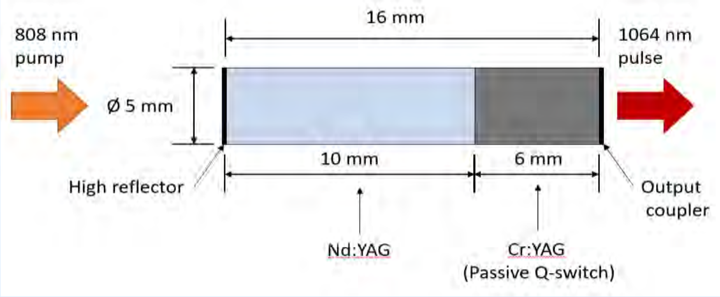


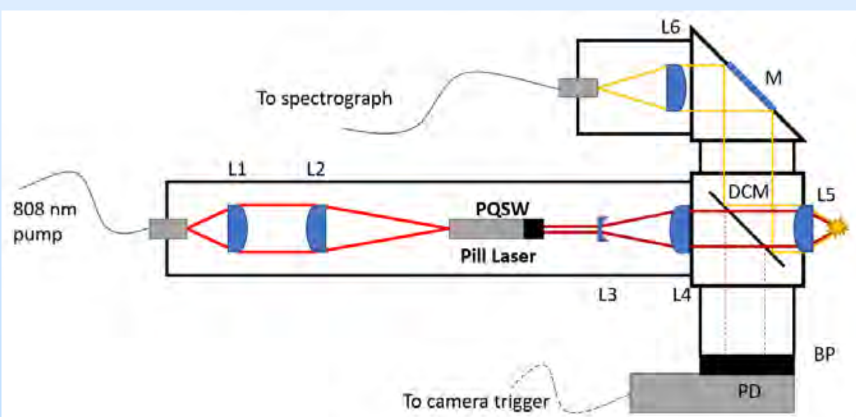
Figure 5: Basic design of the monolithic PQSW Nd:YAG Pill laser. The high reflector is coated directly onto the Nd^{2+} doped YAG and the output coupler is coated onto the Cr^{4+} doped YAG. The two YAG crystals are bonded.

  - Fiber delivers pump pulse and returns spectral signature
  - Laser can be designed to perform either LIBS or RAMAN excitation
  - Laser is 16mm long
  - Entire optical setup can be sealed to withstand pressure and temperature
  - Laser operation is dictated by selection of optical element parameters and tailoring of input pump pulse

Geochemical Monitoring:
Laser Induced Breakdown Spectroscopy (LIBS)

Miniaturized Probe Construction

- Initial prototype constructed around a 30mm optical cage system
- Full operation validated with solids, liquids, and in air
  - Geometry would allow access to 8in pipe
- Second smaller prototype constructed around 16mm optical cage system
  - Geometry would allow access to 4in pipe
  - Challenges with spark production and data quality



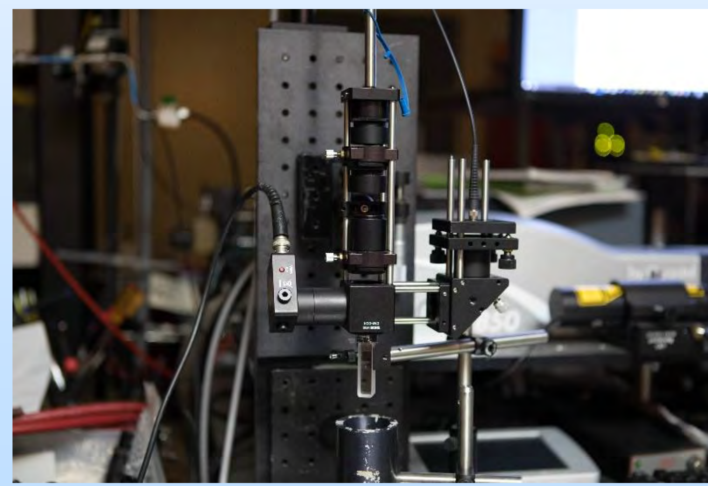


Figure 1: Layout of LIBS sensor head. Pump coupling lenses L1 = 25 mm and L2 = 50 mm, Beam expander L3 = -25 mm and L4 = 75 mm, Aspheric focusing lens L5 = 10 mm, Emission coupling lenses L5 and L6 = 50 mm. DCM = dichroic mirror, M = aluminum mirror, BP = 1064 nm bandpass filter, PD = photodiode.

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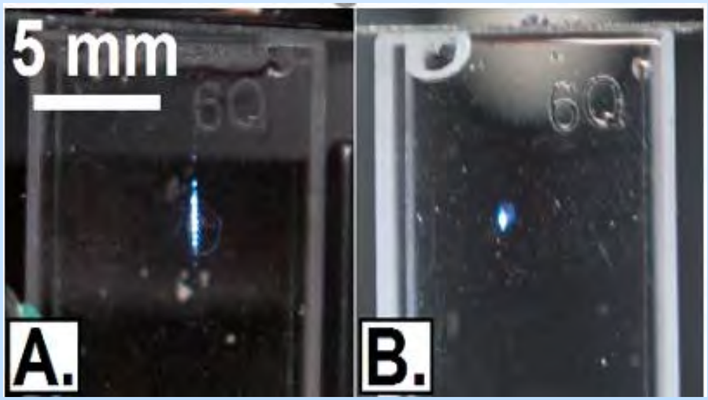
Geochemical Monitoring:
Laser Induced Breakdown Spectroscopy (LIBS)

Challenges Overcome

- Modification of pumping light to activate the laser
  - Increased size of pumped volume inside the active material
  - Improvement of output beam quality (M^2~1.04)
- Modification of output beam size with beam expander
  - Initial long spark production shielded light used for analysis
  - Initial long spark was inconsistent due to extended intensity distribution
- New compact spark due to improved intensity distribution
  - Reduced light shielding and more light available for analysis
  - Perfect consistency in location and time
  - Improved SNR and lower LOD



Geochemical Monitoring:
Laser Induced Breakdown Spectroscopy (LIBS)

Data Collection and Validation

- Calcium, Strontium, Potassium measurement in solution
  - LOD in ppb range (below)
- Europium and Ytterbium measurement in solution
  - LOD 1-2 ppm range
- Europium and Ytterbium measurement in solid form
  - LOD 10-40 ppm (dependent on emission line used)

Table 1: LODs for Ca, Sr, and K.

Element	Line (nm)	LOD[A] (ppm)	LOD (literature) (ppm)		
Calcium	422.7	0.10	0.94[B,†]	0.047[C]	0.13[F]
	393.4*				0.6[F]
Strontium	460.7	0.04	2.89[B,†]		
	421.5*			0.34[D,#]	
	407.8*				0.025[G]
Potassium	766.6	0.009	0.03[B,†]	1.2[E]	
	769.9	0.069			

A – This study, **B** – Gougeuel et. al. 2015 [21], **C** – Pearman et. al. 2003 [22], **D** – Fichet et. al. 2006 [23], **E** – Cremers et. al. 1984 [20], **F** –Knoop et. al. 1996 [24], **G** – Popov et. al. 2016 [25], * - Lines showed self-absorption over the concentration ranges used in this study, **†** - NaCl solution matrix, **#** - LIP on liquid surface

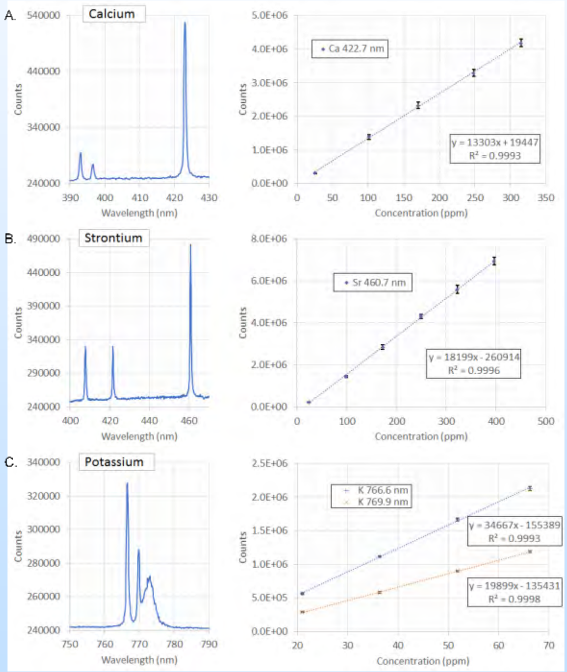


Figure 1: Emission spectra and calibration curves for the: **A** - Calcium (422.7 nm line), **B** - Strontium (460.7 nm line), and **C** - Potassium (766.6 and 769.9 nm lines). The intensities for the calibration curves are the integrated intensities of the emission lines. Cation concentration for the emission spectra are 25.1 ppm Ca, 24.1 ppm Sr, 5.2 ppm K. Note the broad 773 nm peak interfering with the potassium spectrum. This peak is also present in DI water.

Accomplishments to Date

- Field deployment of commercial sensors is clarifying the baseline information and methodologies for new tools under development
- Selective and sensitive CO_2 sensing layers have been developed and demonstrated based on metal-organic frameworks
- Efforts towards field deployment have been initiated including (1) optimizing sensor layers for aqueous applications, (2) packaging and testing under application relevant conditions
- Sensing layer modifications to improve hydrophobicity have improved CO_2 sensing performance, more work on-going
- Initial LIBS probe design tested and validated, and data acquisition has been performed to demonstrate performance
- Weatherproof probe underway and flow through lab is in permitting
- 2 patents pending (LIBS), and 2 patents awarded with several other in preparation (Fiber optic)

Lessons Learned & Synergy Opportunities

Lessons Learned

– Sensing layer stability and response in high water vapor conditions requires additional sensing layer development

– Manipulation of LIBS laser pumping geometry and output to improve performance and consistency

Synergy Opportunities

– Opportunities exist to leverage on-going work in wellbore chemical sensing under SuBTER research efforts within NETL R&IC

– Other geochemistry efforts in the Carbon Storage program can provide insights to application relevant levels / performance metrics

– Optical fiber sensor efforts by other teams on physical parameter monitoring can be used to aid and accelerate field deployments

Synergy Opportunities

- Continued field-based collaboration to test new geochemical monitoring techniques and tools under different CO_2 storage conditions (e.g. FO coated sensors)
  - Natural analogs
  - Controlled release sites
  - EOR field systems

NETL researcher, Hank Edenborn (NETL) at the Brackenridge Field Site (Austin, TX)

Project Summary

- Geochemical monitoring methods/tools are being field validated & baseline signals interpreted
- Information gained from knowledge of CO_2 storage systems is being used to inform development of novel in-situ chemical sensing tools
  - NDIR for CO_2 in shallow systems: natural analog successfully tested, CCS site deployment underway
  - LIBS – lab validated, moving towards field prototype
  - MOF coated FO sensor for direct chemical sensing - lab validation in progress, field testing in upcoming 2 yrs

Appendix

Benefit to the Program

- Program Goals:
  - Validate/ensure 99% storage permanence.
  - Develop best practice manuals for monitoring, verification, accounting, and assessment; site screening, selection and initial characterization…
- Project benefits:
  - *There is a need to be able to quantify leakage of* CO_2 *to the near surface and identify potential groundwater impacts. This project works to develop a suite of complementary monitoring techniques to identify leakage of* CO_2 *or brine to USDW's and to quantify impact.*

Organization Chart

NETL
Technical Portfolio Lead
Angela Goodman

NETL
Task Technical Coordinator
Christina Lopano

NETL (PI)
Hank Edenborn

NETL (PI)
Paul Ohodnicki

AECOM
Ki-Joong Kim

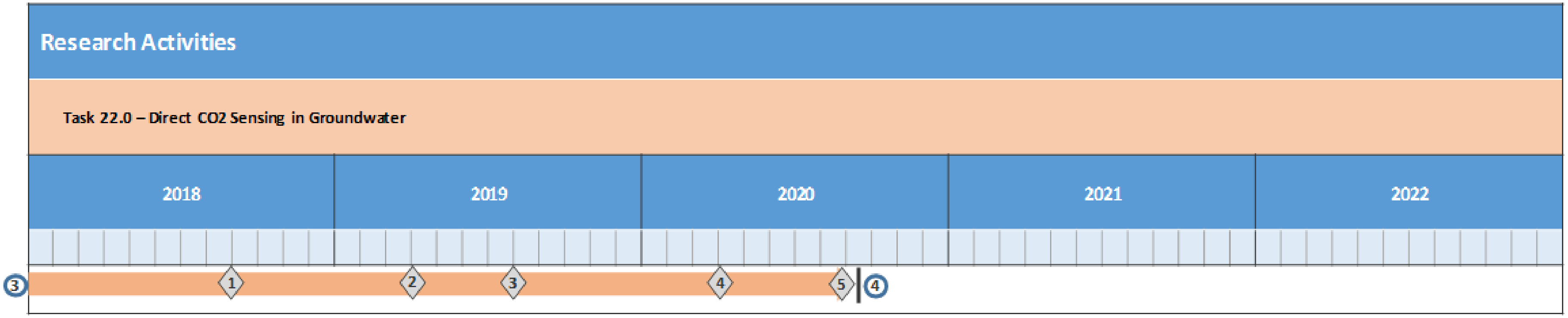
NETL (PI)
Dustin McIntyre

AECOM
Dan Hartzler

Applied Spectra
Jong Yoo
Chunyi Liu

Task 22 Direct CO_2 Sensor Schedule

Direct CO_2 Sensing in Groundwater (PI: Hank Edenborn)



Milestones

1. Deployment of telemetry system for groundwater well
2. Presentation summarizing 6 months field data
3. Deployment of multiple well telemetry system
4. Presentation summarizing 6 months field data
5. Journal publication summarizing total field study

Go / No-Go

Key Accomplishments/Deliverables	Value Delivered
1. Present data summarizing hourly carbon dioxide measurements in groundwater well over 6 months (03/2019) 2. Present data summarizing carbon dioxide measurements collected from an array of groundwater wells (03/2019) 3. Publish final results in scientific publication (08/2020)	• Demonstrate and validate scientific method for real-time monitoring of carbon dioxide concentrations in groundwater at carbon storage field site.

Chart Key

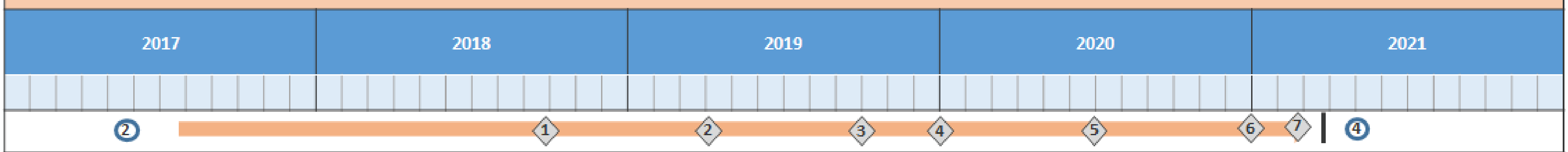
\# TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Task 23 Fiber Optic Sensor Schedule

Distributed Fiber Optic based CO_2 Sensors for Carbon Storage Applications (PI: Paul Ohodnicki)

Research Activities

Task 23 – Distributed Fiber Optic Based CO2 Sensors for Carbon Storage Applications



Milestones

1. Establish a test facility and packaging approach for fiber sensor testing at NETL on-site "field testing" laboratory
2. Demonstration of a water mitigated vapor cross-sensitivity for a modified MOF or alternative sensor layer
3. Benchmarking of fiber optic chemical sensing performance relative to commercial CO_2 NDIR sensor
4. Development of packaging and proposed procedures for a field validation effort in shallow groundwater
5. Successful completion of first shallow-ground water field test
6. Successful completion of second shallow-ground water field test
7. Plans developed for extension to wellbore and geological sequestration deployment of distributed fiber optic sensing technology including new sensing materials, interrogator, and packaging development.

Go / No-Go

Impact

Key Accomplishments/Deliverables	Value Delivered
1. Paper submitted outlining mitigation of water vapor cross-sensitivity for CO_2 sensing. (3/31/2019) 2. Developed plans for field testing for review and discussion. (12/31/2019) 3. Results of field testing of CO_2 in shallow ground waters and benchmarking with commercially available CO_2 NDIR sensor. (12/31/2020)	• A fiber optic based CO_2 sensor probe compatible with distributed interrogation to be initially demonstrated in shallow ground waters but ultimately capable of extension to wellbores and embedded sensing in sequestration sites.

Chart Key

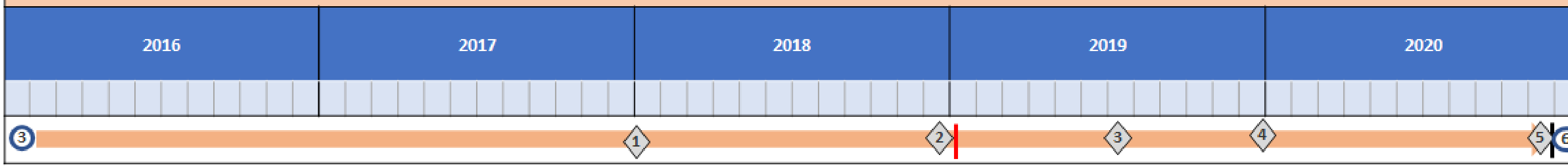
\# TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Task 24 LIBS flow Schedule

In-Situ Subsurface Fluid Measurements with Laser Induced Breakdown Spectroscopy (LIBS) (PI: Dustin McIntyre)

Research Activities

Task 24.0 – In Situ Subsurface Fluid Measurements with Laser Induced Breakdown Spectroscopy (LIBS)



1. Journal Manuscript showing feasibility of measuring dissolution at pressure
2. Optical data validation. White paper describing benefits
3. Journal Manuscript outlining initial experimentation
4. Flow experiments performed with real and/or manmade subsurface materials
5. Journal Manuscript outlining detailed flow experiments in in-situ conditions

Chart Key

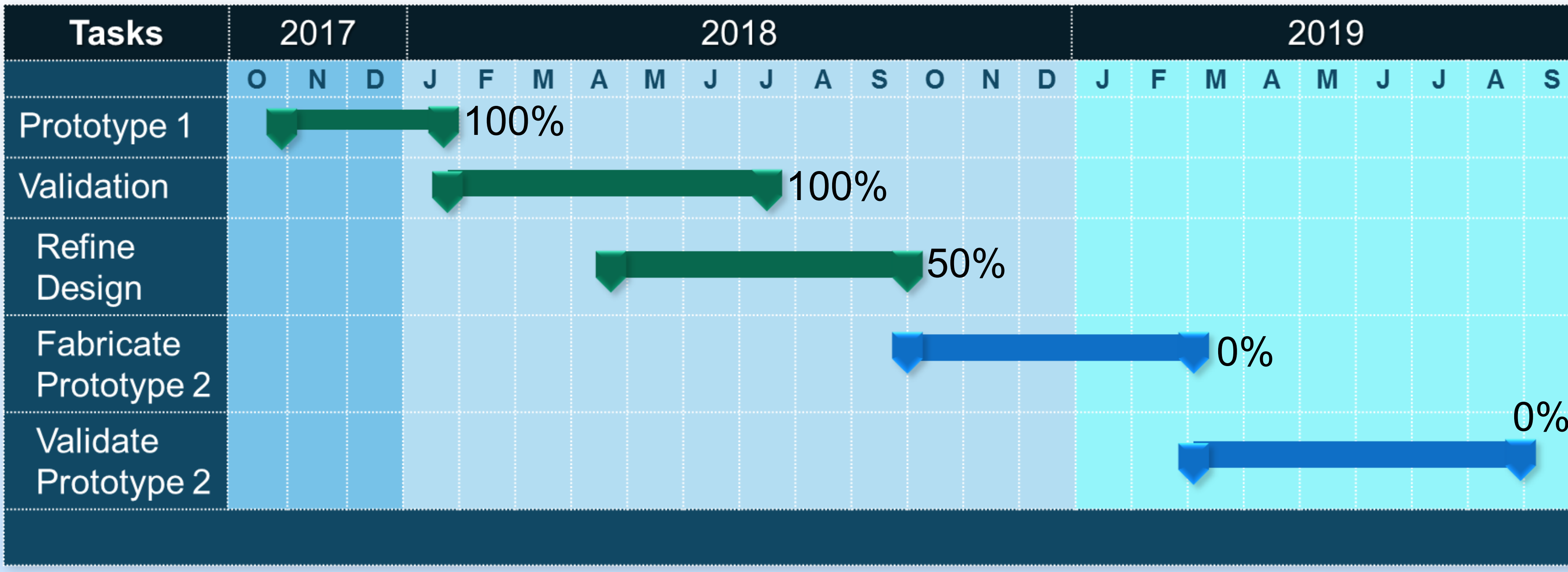
\# TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Go / No-Go

Impact

Key Accomplishments/Deliverables	Value Delivered
2017: Concurrent LIBS flow cell measurements on the lab bench preparing for field deployment. (Goueguel, C., Bhatt, C., Jain, J., Lopano, C., McIntyre, D., "Quantification of metal ions in high-pressure CO_2-water solutions by underwater laser-induced breakdown spectroscopy," Manuscript in review) 2 Patent applications in progress	• Laboratory based system for measuring simulated subterranean water chemistry under flowing conditions. System will allow for the high quality measurement of elemental species in ground water before and after flowing through either natural or manmade materials (rocks). • System can be used to mock-up field studies with temperature, pressure, and flow conditions prior to deployment.

TCF Schedule



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