Real-time Sensor Technologies for H_2 Subsurface Storage and Transportation Monitoring

NATIONAL ENERGY TECHNOLOGY LABORATORY

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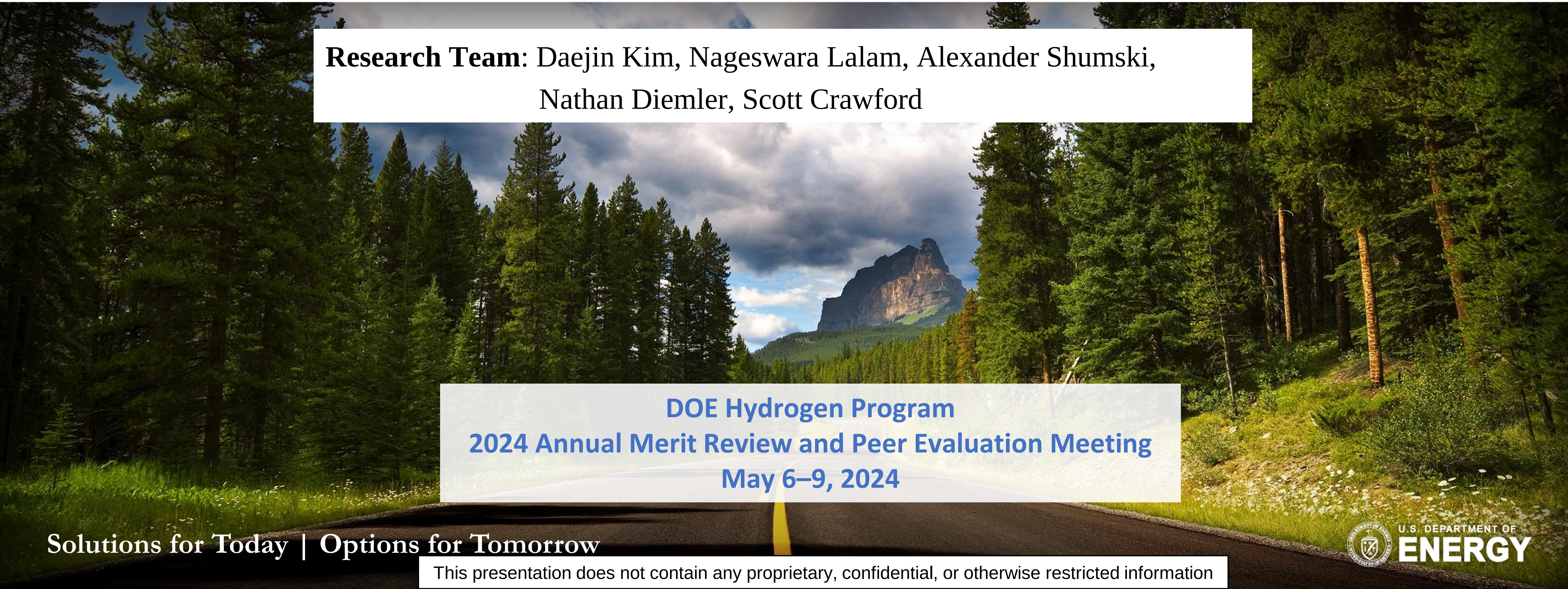

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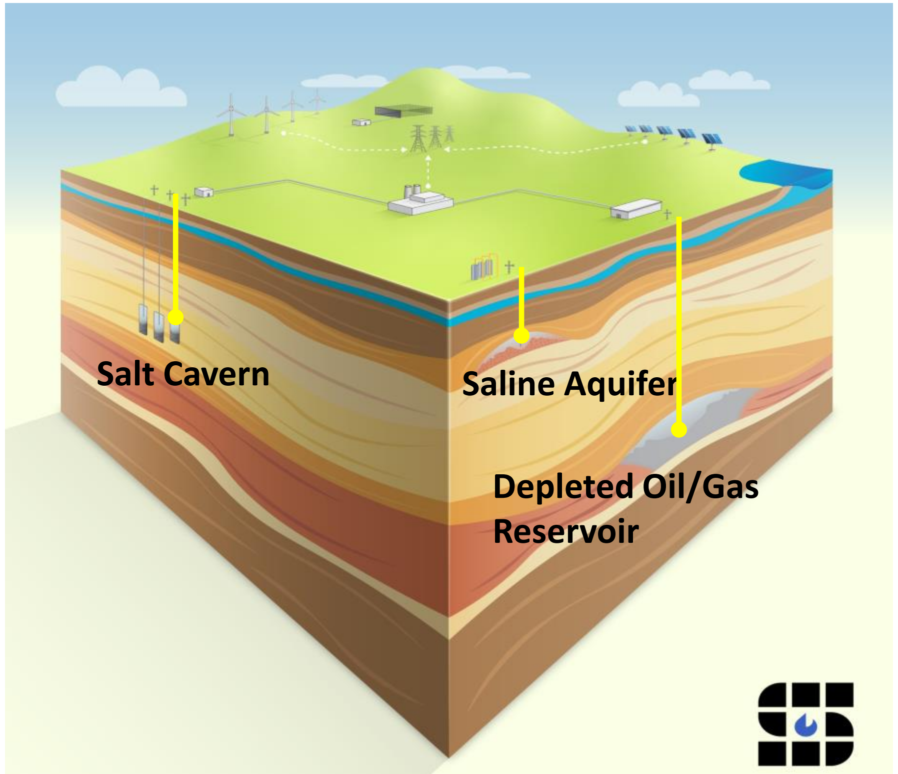
DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting
May 6–9, 2024

Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

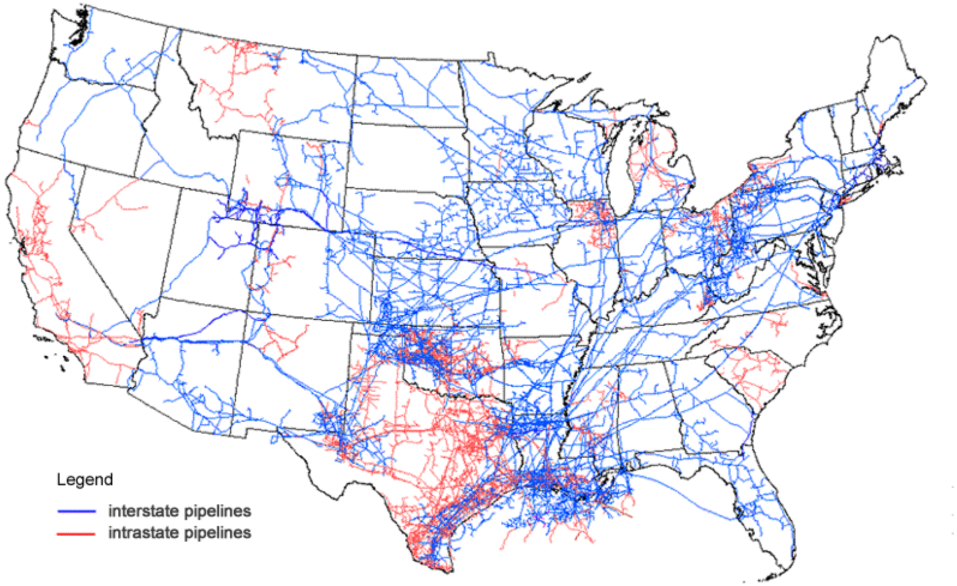
Enabling large-scale H_2 storage and transportation

Subsurface Hydrogen Storage



(Source: https://edx.netl.doe.gov/shasta)

H_2 or HyBlend Transportation via NG Infrastructure



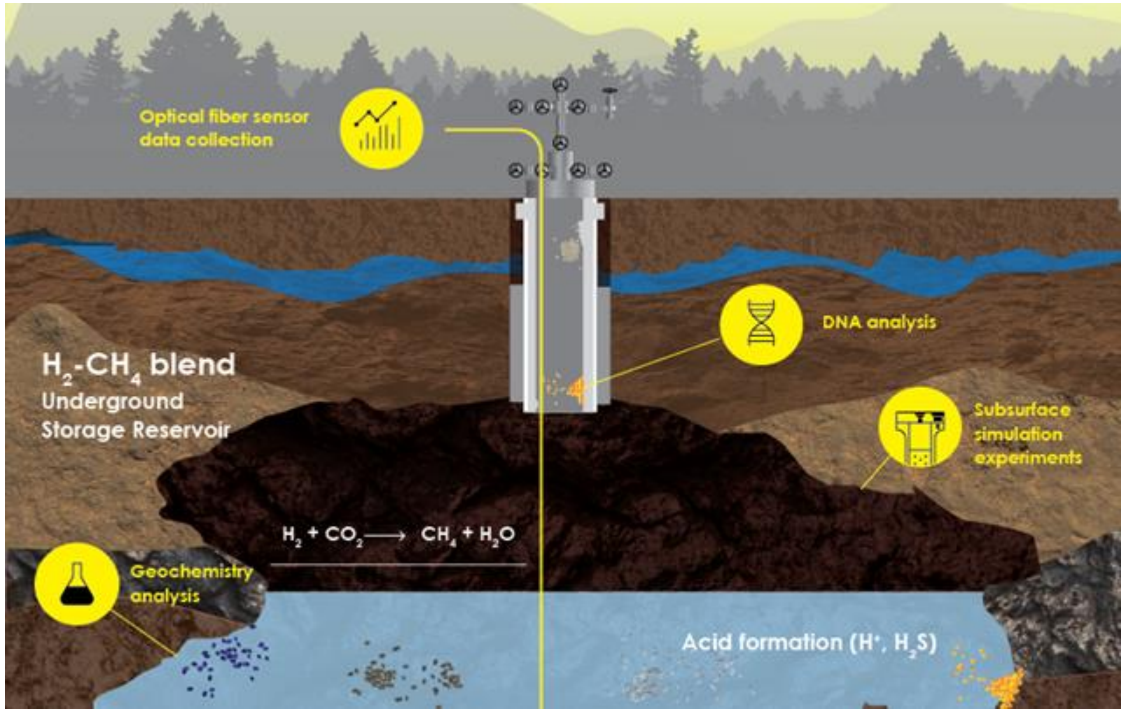
Source: U.S. Energy Information Administration, *About U.S. Natural Gas Pipelines*

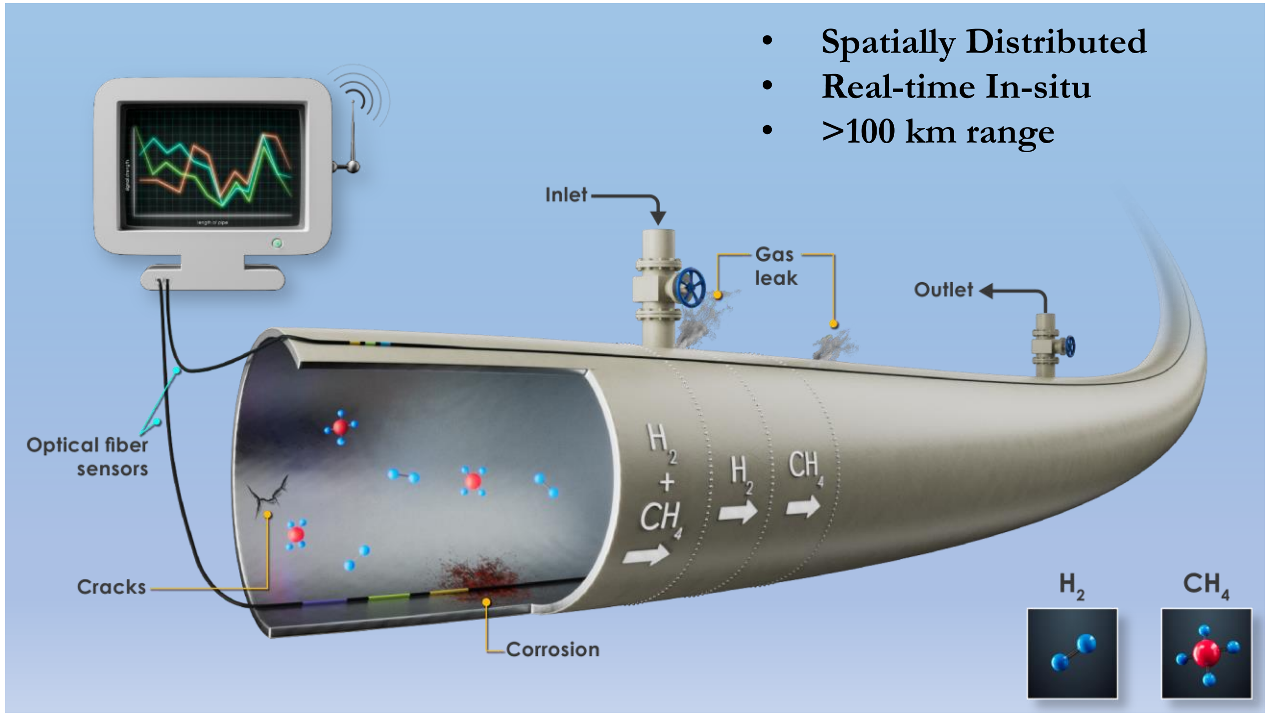
- Subsurface H_2 storage costs **three to five times less** than above-ground tank storage.
- Leveraging the existing natural gas (NG) pipeline infrastructure provides a viable and cost effective option for large-scale H_2 transportation

Real-time Sensors for H_2 Subsurface Storage and Transportation Monitoring

SHASTA
Subsurface Hydrogen Assessment, Storage, and Technology Acceleration

Natural Gas Decarbonization and Hydrogen Technology FWP (NGDHT)





Project Period: 04/2021-04/2024

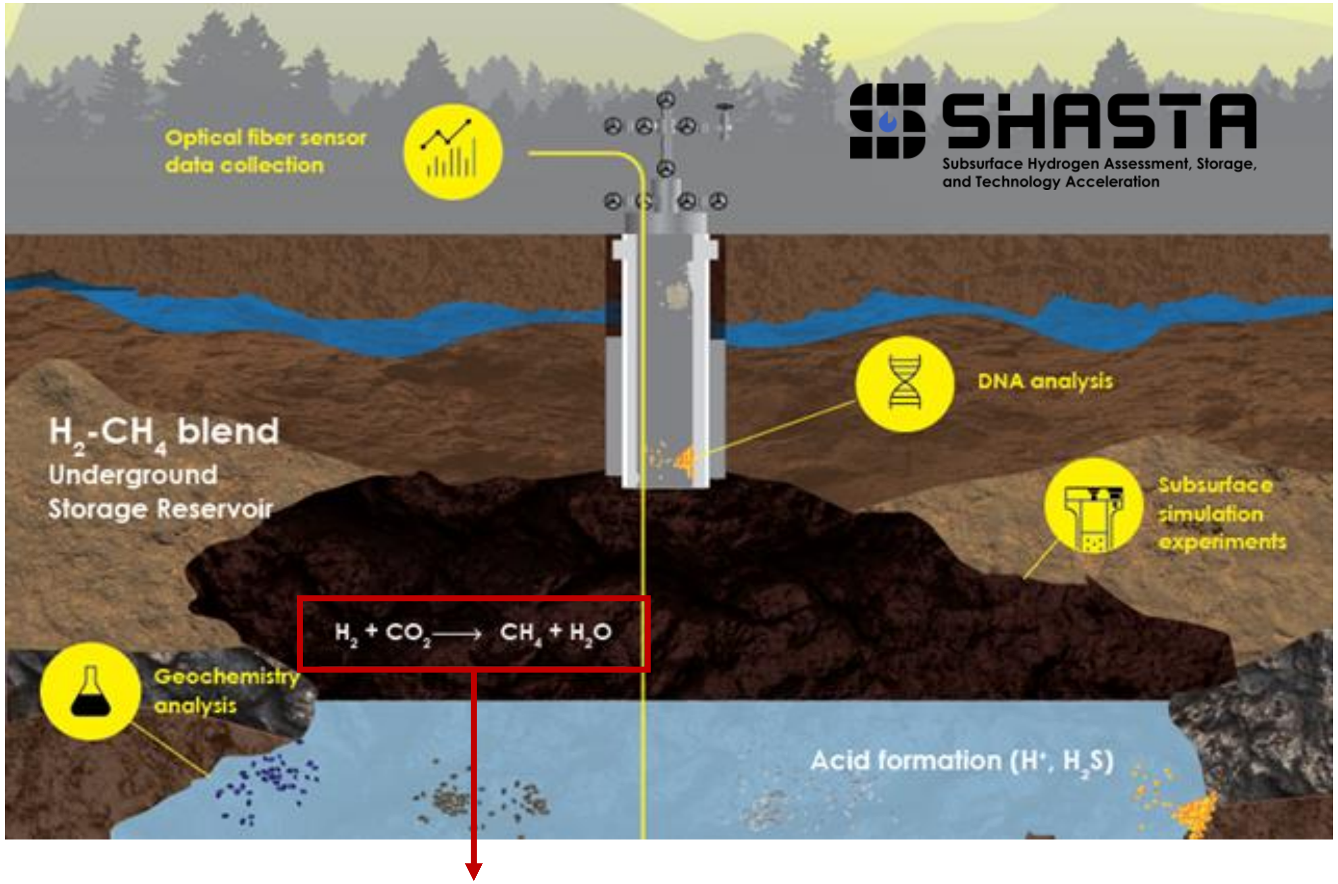
- Early detection of hydrogen leaks to ensure safety and reliability.
- Wellbore and pipeline integrity monitoring to prevent catastrophic failures.

Project Objectives

- In-situ optical fiber sensors for real-time monitoring of **<u>hydrogen, methane, and chemical parameters</u>** at subsurface hydrogen storage conditions

Impact on Subsurface Hydrogen Storage

- Determine microbiological H_2 consumption/depletion and pH change
- Identify well integrity risks
- *Real-time* vs Periodic Sampling
- *In-situ* vs Ex situ



- Microbial conversion of hydrogen in subsurface storage wells
- **Need for real-time monitoring** of gas composition and geochemical conditions.

State of the Art of Hydrogen Sensors

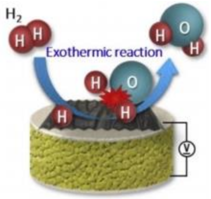
(*Chemistry Select 2020, 5, 7277-7297*)

(**P**: Physical change, **A**: Advantage, **D**: Disadvantage)

H_2 Sensors

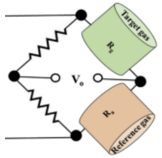
Catalytic

P: temperature, resistance
A: robust, stable, wide operating temperature range
D: requires O_2, high power consumption



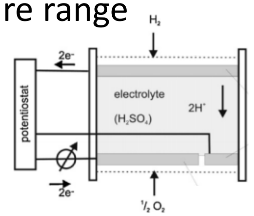
Thermal

P: thermal conductivity, resistance
A: fast response, low cost, simple construction
D: high lower detection limit, cross-sensitive to He



Electro-Chemical

P: electric current, voltage
A: sensitive, working at high temperature
D: low life, narrow temperature range

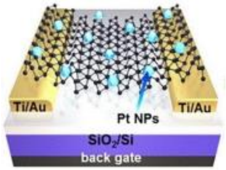


Resistive

P: resistance
A: high sensitivity, fast response
D: poor selectivity, interfering with humidity

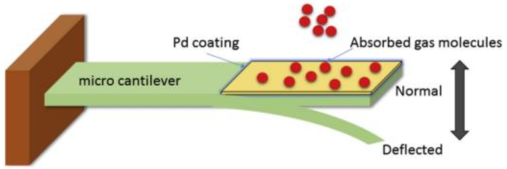
Work Function

P: voltage, current, capacitance
A: small size, high sensitivity and selectivity
D: susceptible to drift, saturation at modest concentrations



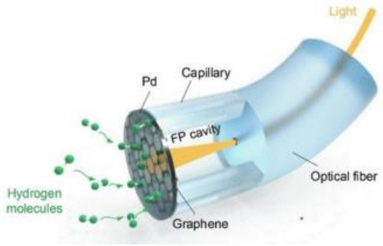
Mechanical

bending, curvature: **P**
micromachinable, small size :**A**
slow response, aging effect :**D**



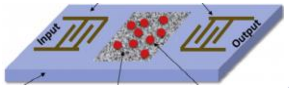
Optical

transmission, reflectance, wavelength: **P**
fast response, no source of ignition :**A**
Interference from ambient light :**D**



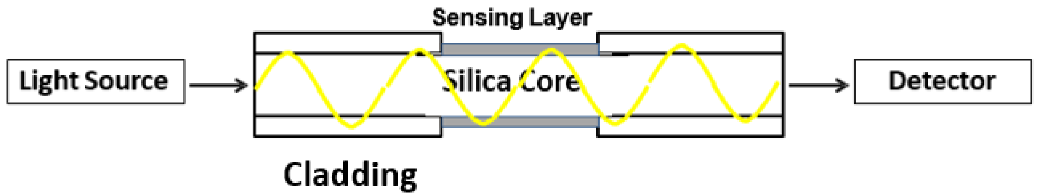
Acoustic

frequency, wave velocity, time: **P**
high sensitivity, fast response :**A**
interference from humidity, drift :**D**

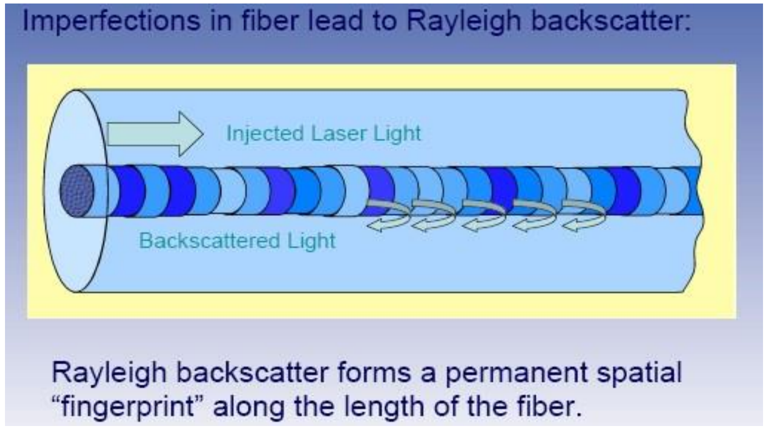


Approach: Optical Fiber Sensors

Sensing Principle : Evanescent Wave Sensors



Distributed Sensing

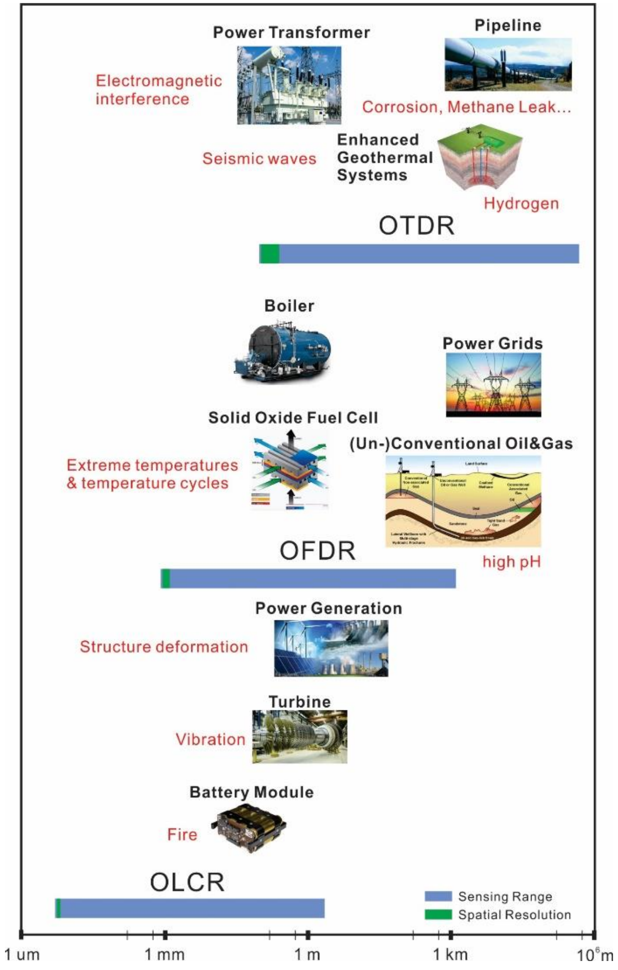


Advantages of Optical Fiber Sensors (OFS)

- **Improved safety** in the presence of flammable gases compared to electrical based sensors
- **Stable** in subsurface harsh environments
- Small size and flexibility
- Long reach, light weight
- Can be **functionalized** for targeted parameters through functional materials
- Compatible with **distributed or multi-parameter** interrogation.

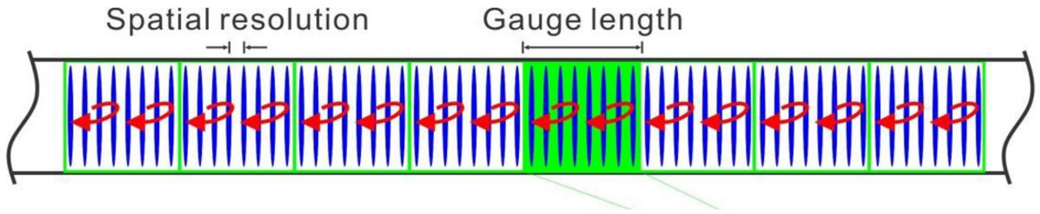
- **Need functional sensitive materials that enable H_2, CH_4, and geochemical sensing (e.g. pH and corrosion), which are compatible with high pressure high temperature and humid conditions in subsurface.**
- **Spatially distributed sensing can *identify and locate* the hydrogen leaks along a long-distance pipe.**

NETL Capability in Distributed Optical Fiber Interrogator Development

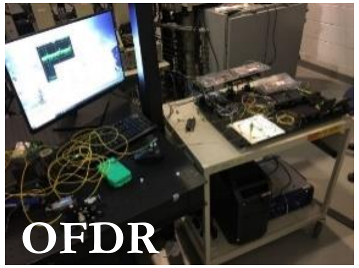


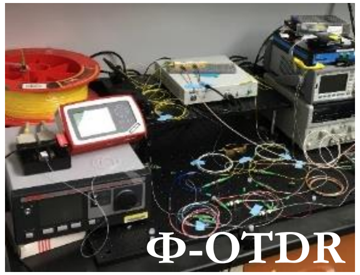
Ref: Lu et al, Appl. Phys. Rev. 6, 041302 (2019)

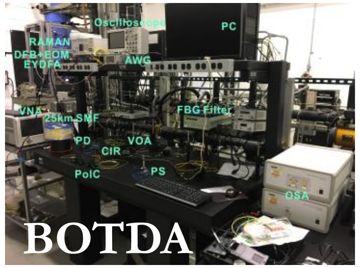
In-House NETL Distributed Optical Fiber Sensor Interrogators



Technology	Sensing Range	Spatial Resolution	Measurement Time	Fiber Type	Sensing Performance
Coherent Rayleigh OFDR	m – km	mm – cm	seconds	SMF	Temperature, strain, vibration, chemical sensing
Coherent Rayleigh OTDR	km	m	seconds	SMF	Acoustic wave, vibration
Brillouin OTDR/BOTDA	> 100 km	cm – m	minutes	SMF	Temperature, strain,







Multiple Distributed Optical Fiber Sensing Platforms Have Been Developed to Enable Structural Health Monitoring of Natural Gas Pipeline, particularly for Corrosion Onset and Gas Leak Detection.

Subsurface Hydrogen Storage Conditions

High-Pressure High-Temperature (HPHT), Humidity, Mixed Gas, and Dissolved Solids

- Stable at ~80°C and ~1000 psi (up to 4000 psi)
- Hydrogen concentration: 5% to 100%
- Capable of surviving mechanical insertion into high pressure wellbore
- Microbially active environments
- pH ranging from ~4 -10
- High humidity environments
- Sensors must be compatible with mixed $CH_4/CO_2/H_2/H_2O$ conditions.

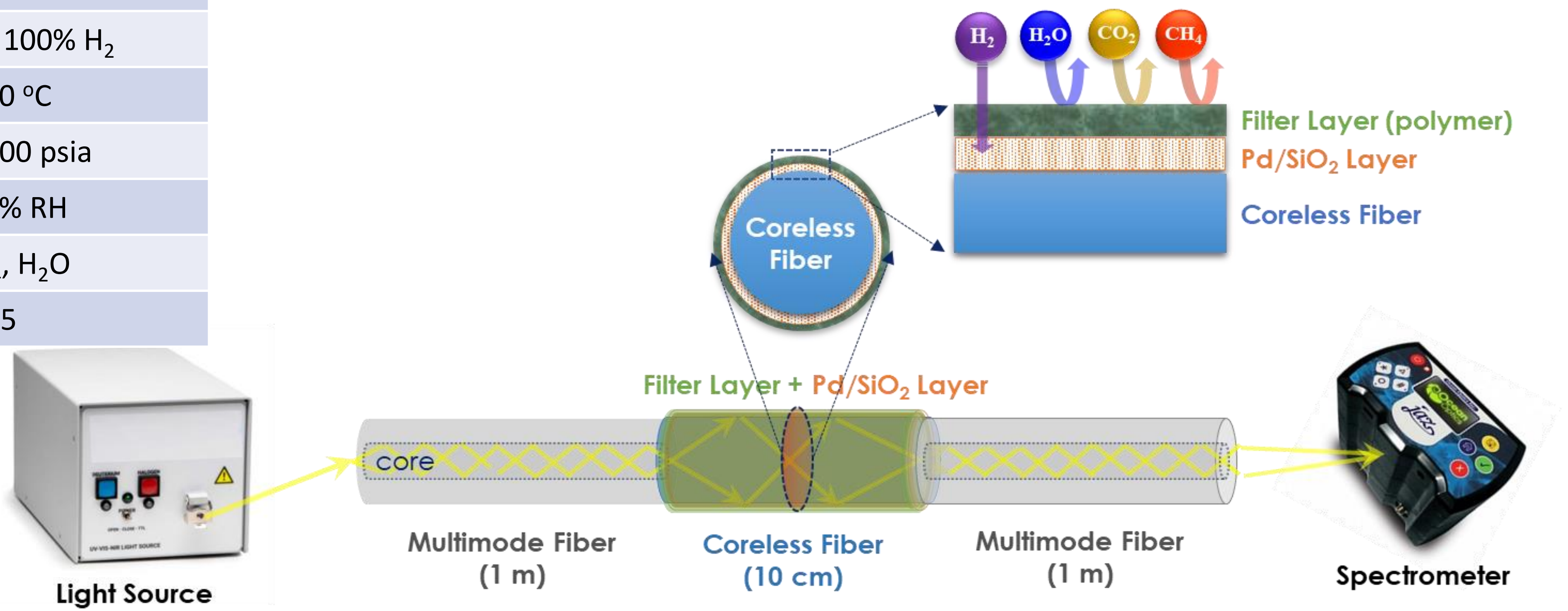
Application	Depth	Average Temperature	Pressure	pH Range	Dissolved Solids	Common Ions
H_2 and H_2/CH_4 Blend Storage	200-2000 m	25-100 °C	5-30 MPa	4-9.5	10,000-70,000 mg/L	Sulfides, CO_2/Carbonate, Cl^-, Na^+, K^+, H_3O^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, $Fe^{II/III}$

(Goodman Hanson et al., 2022; Bérest, 2019;Tarkowski, 2019; Zivar et al., 2021; Muhammed et al., 2022; Pannekens et al., 2019)

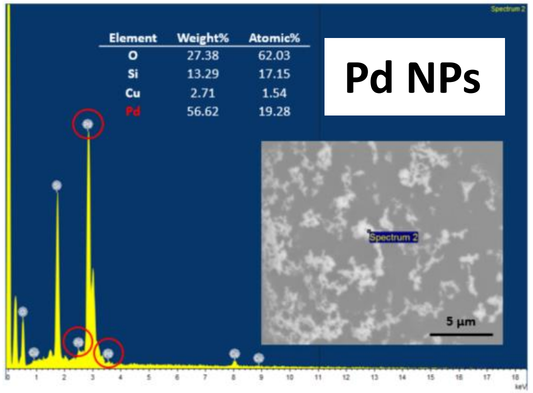
Lack of existing hydrogen sensors compatible with HPHT.

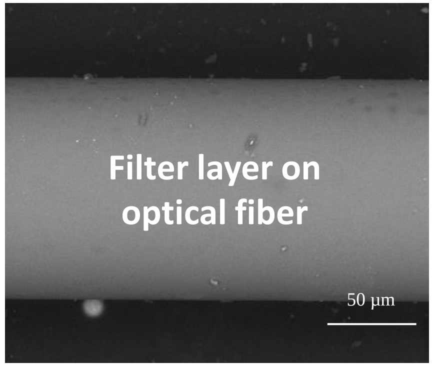
Progress: Optical Fiber H_2 Sensor

Hydrogen Sensor Performance Specifications	
Measurements	Light transmission based
Concentration	100 ppm to 100% H_2
Temperature	20 to 80 ^oC
Pressure	14.7 to 1000 psia
Humidity	0 to 100% RH
Comparability	CO_2, CH_4, H_2O
Current TRL	4 to 5

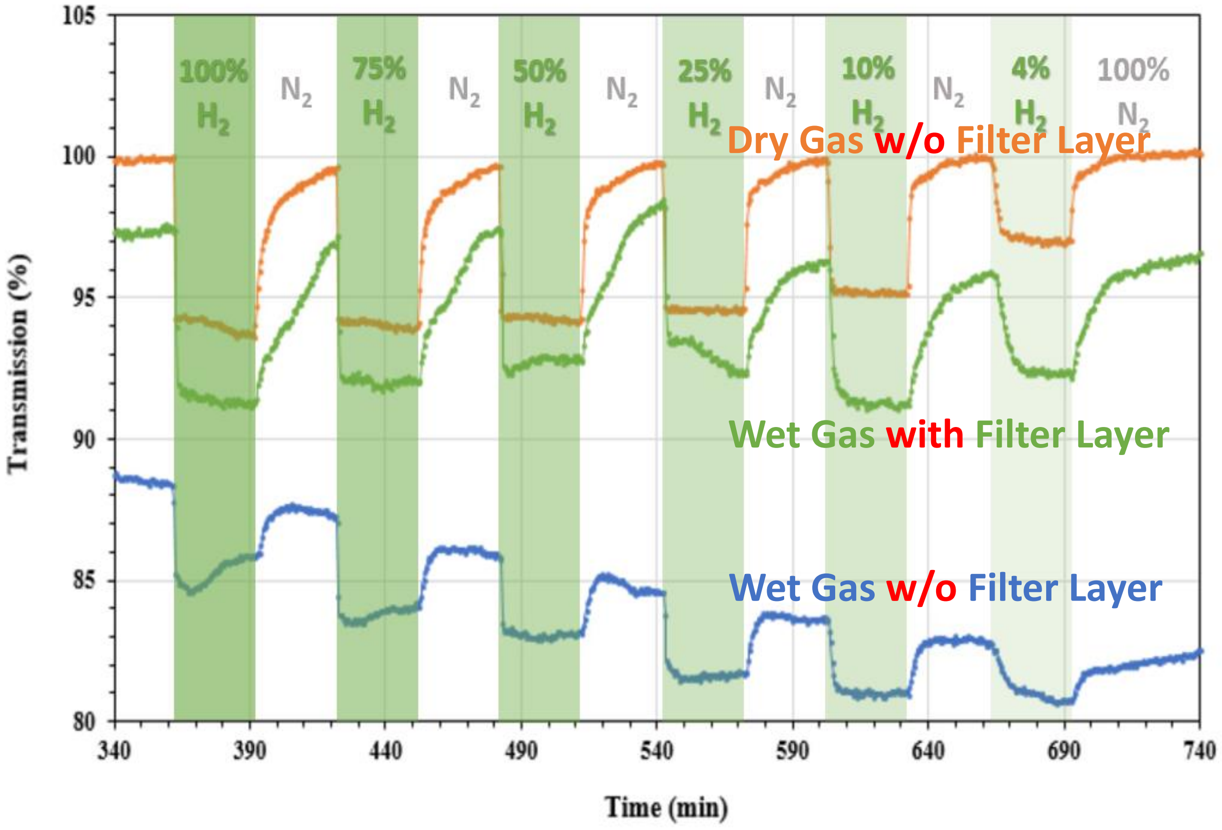


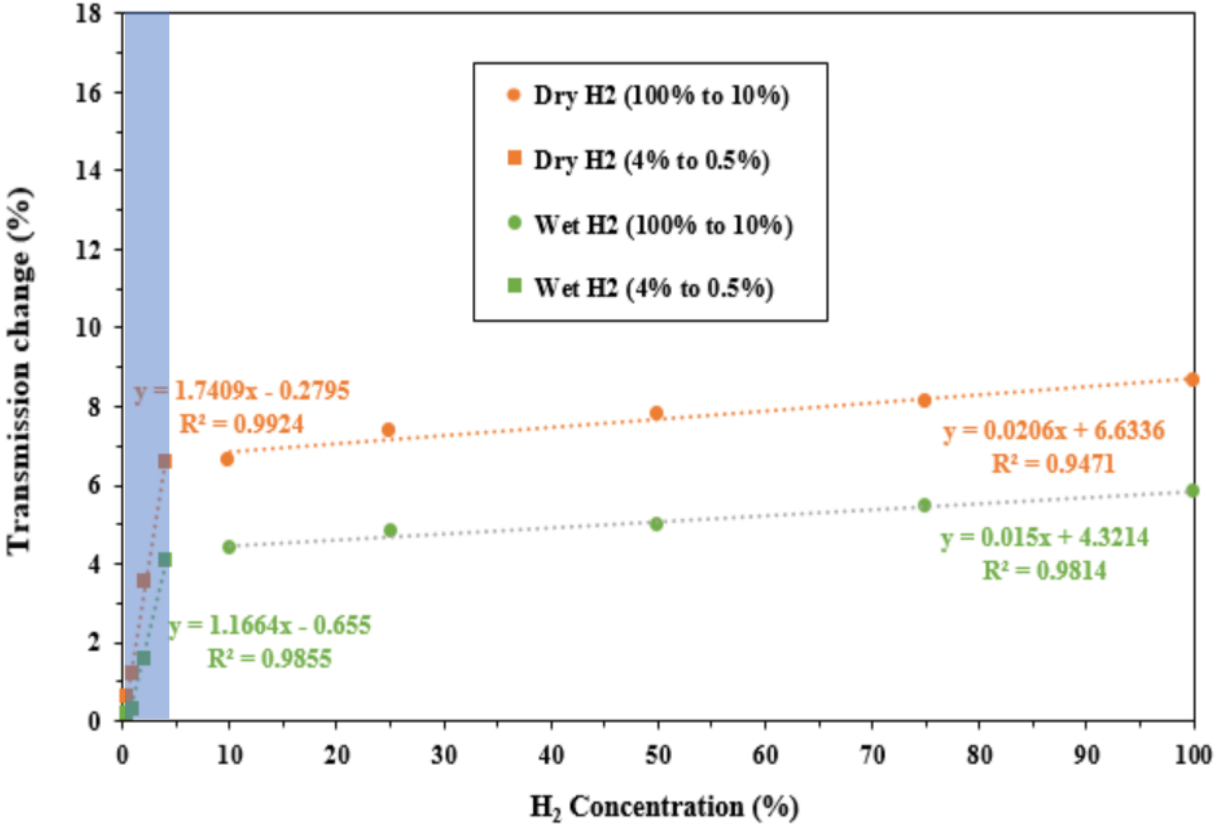
- Pd nanoparticle (NP) incorporated SiO_2 coated optical fiber sensor was developed for H_2 sensing.
- A new filter layer was overcoated on the sensing layer to increase selectivity and mitigate humidity interference.





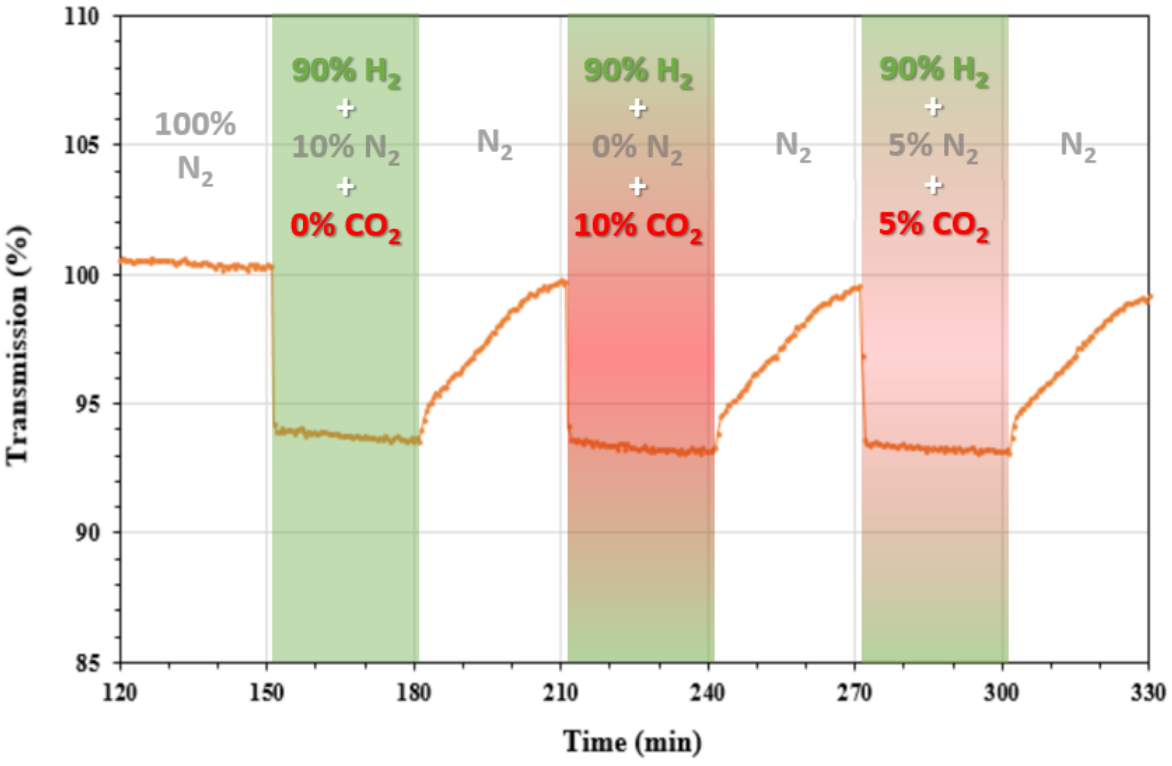
Optical fiber H_2 sensor under humid conditions

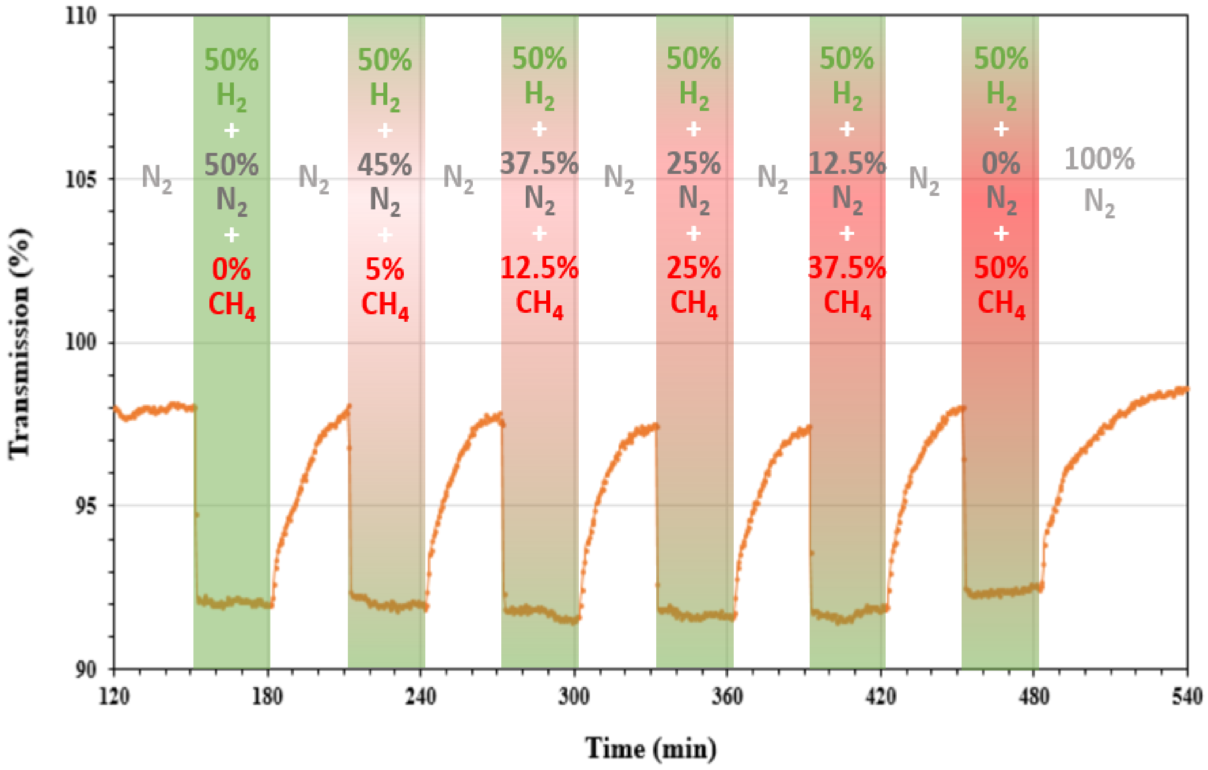




- The new filter layer has significantly mitigated humidity effect on hydrogen sensing.
- H_2 sensing calibration plots under humidity conditions were obtained for a wide range of 0.5% to 100%.

Optical fiber H_2 sensor has no cross-sensitivity to CO_2 and CH_4

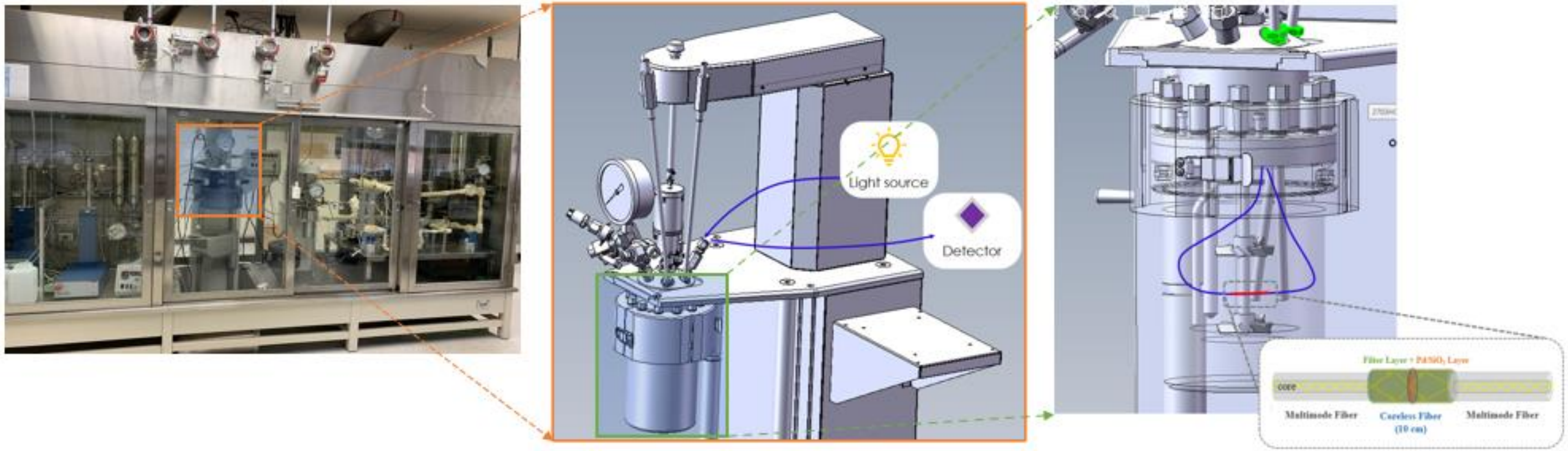




- In order to guarantee a minimum reservoir pressure, the reservoir is filled with a **cushion gas** such as CO_2, N_2, or possibly NG.
- Under 99% relative humidity, the optical fiber H_2 sensor with the filter layer has shown negligible effects from CO_2 or CH_4.

Sensor Tests in Simulated HPHT wellbore conditions with Microbial Samples

Subsurface Sensor Development Reactor (SSDR)



T: 80 ^oC; P: ~850-1000 psi.

SSDR capability:

Automation with LabView: Batch and Flow-through Modes;

High-Temperature High-Pressure (HTHP): up to 450 ^oC, 4500 psi;

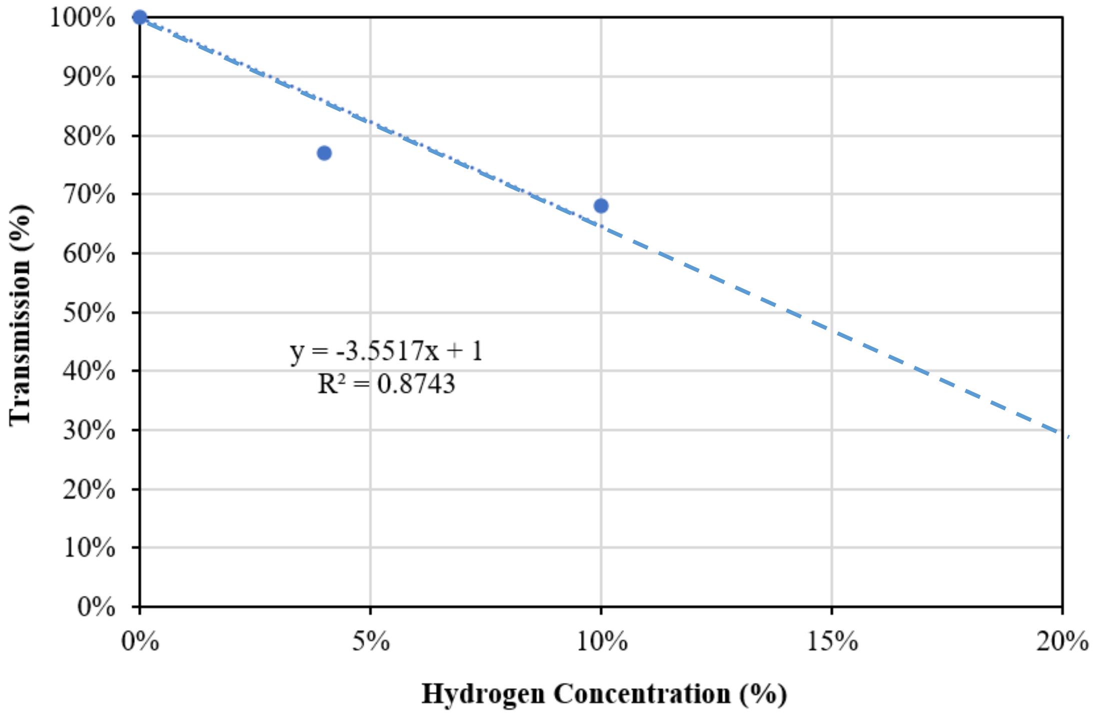
Multi-phase: aqueous, gas, supercritical;
Gas: H_2, CO_2, CH_4, N_2, Air, H_2S.

Type	Liquid Phase	Gas Phase	Days
Control	DI	CH_4 or 80/20 CH_4/H_2	3
Abiotic:CH4	Filtered PDR	CH_4	1,3,7
Biotic: CH4	Unfiltered PDR	CH_4	1,3,7
Abiotic:H2+ CH4	Filtered PDR	80/20 CH_4/H_2	1,3,7
Biotic: H2+ CH4	Unfiltered PDR	80/20 CH_4/H_2	1,3,7

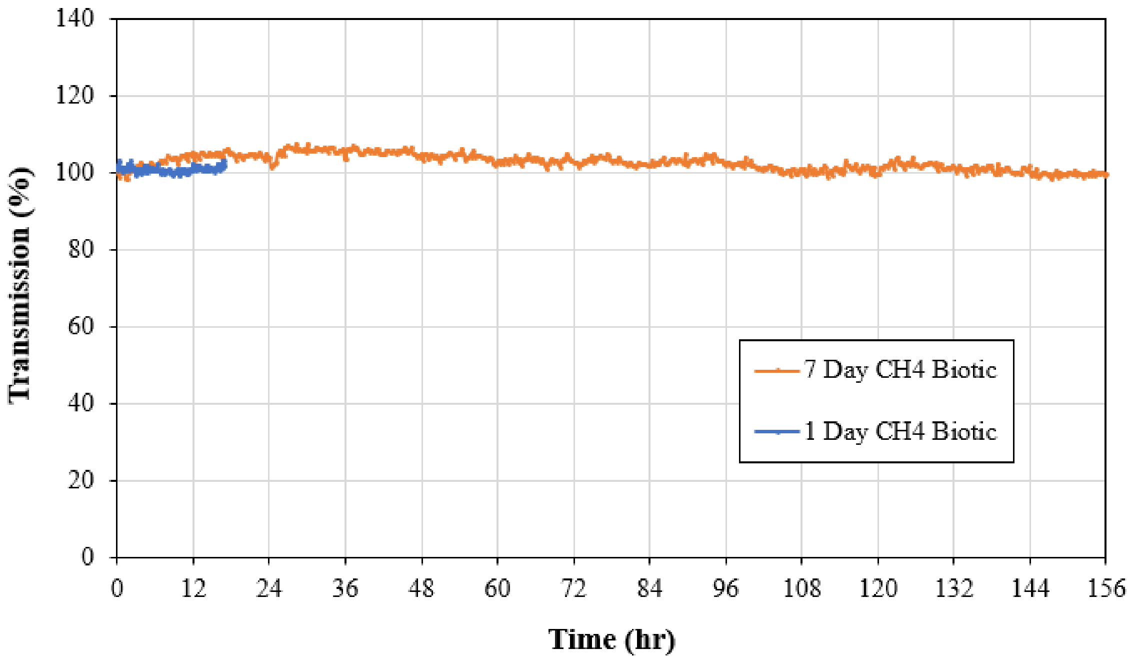
PDR = Playa Del Rey wellbore fluid provided by SoCalGas

Hydrogen Sensing Results in HPHT Microbial Tests

Calibration Plot at 80 °C, 1000 psi



Example: 100% CH4 Biotic condition



- Calibration plot of hydrogen sensor at 80 °C, 1000 psi. More data are needed for wider range calibration.
- Decrease of light transmission indicates increase in hydrogen concentration.
- No hydrogen concentration changes were detected in 100% CH_4 biotic conditions.

Real-time Hydrogen Concentration Monitoring

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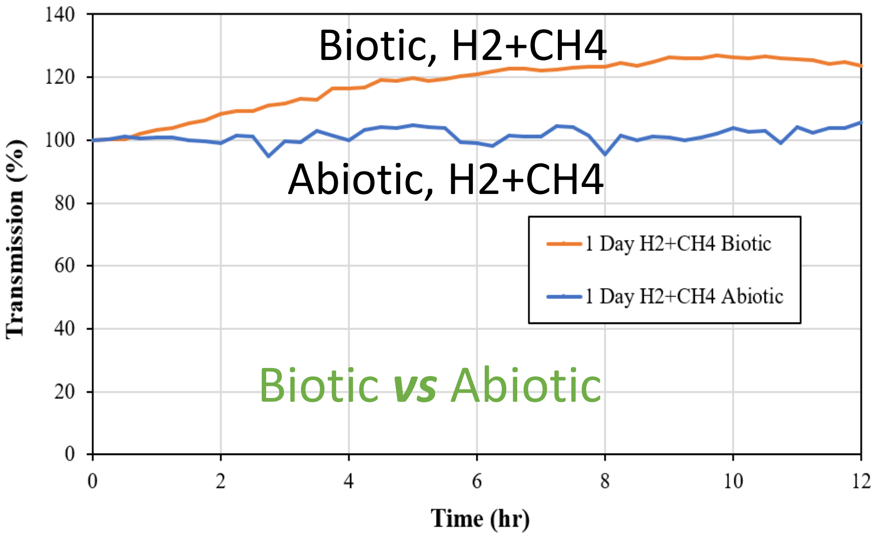
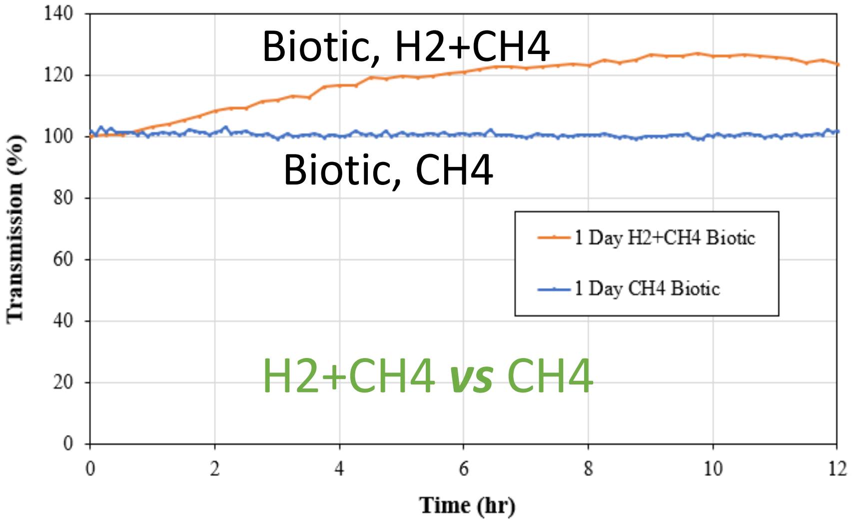
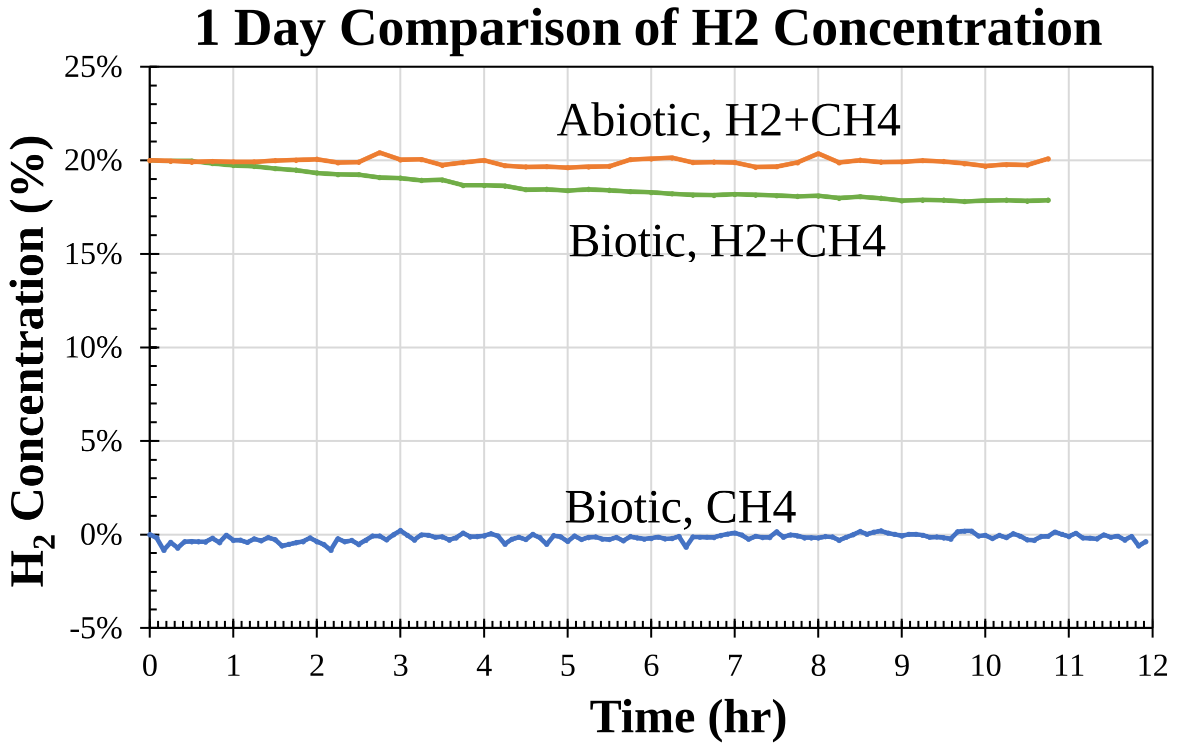
Light Transmission Measurements

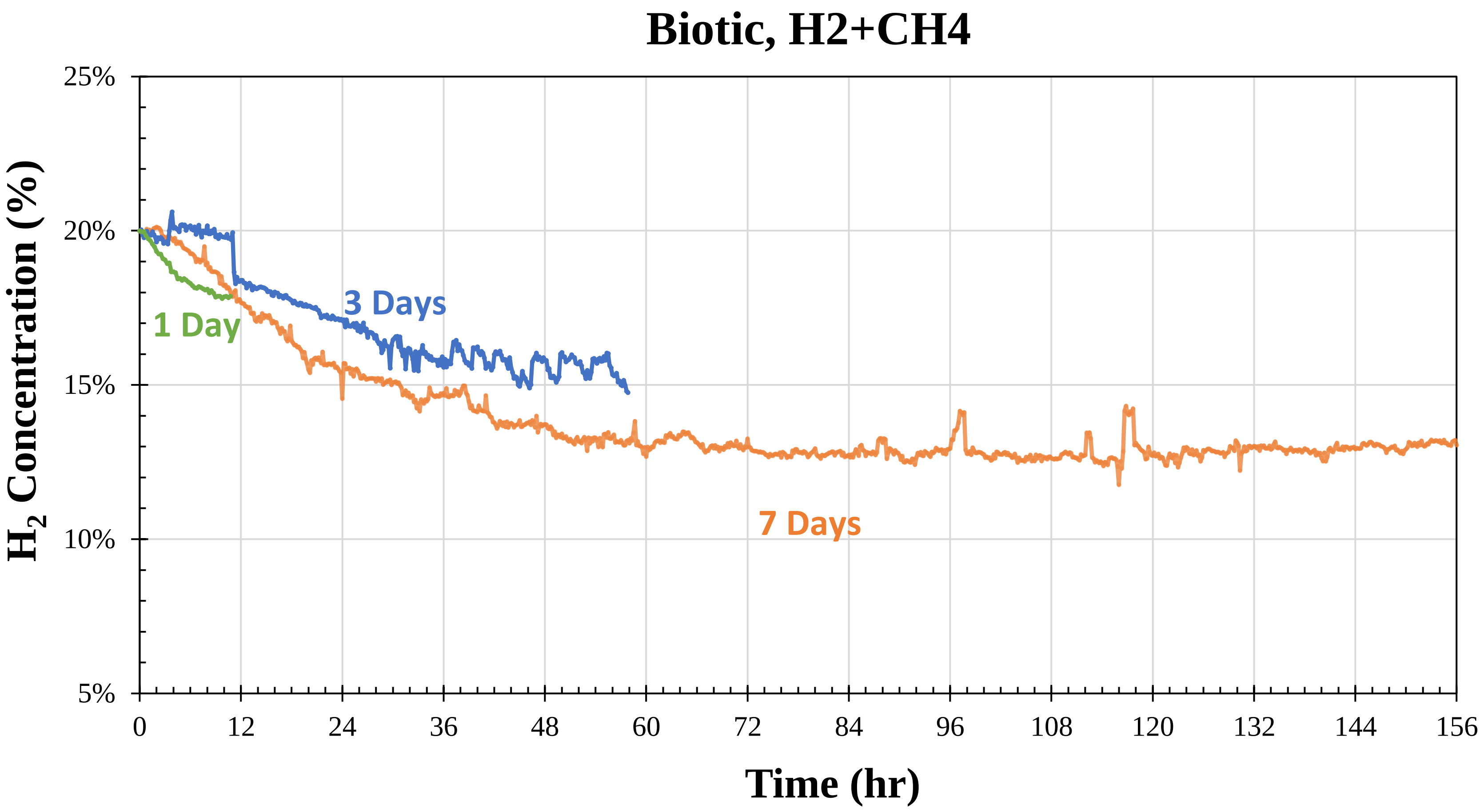






- In biotic conditions, optical fiber hydrogen sensor detected decrease in hydrogen concentration by 2% in 11 hours in H2+CH4 blend.
- The sensor didn't detect hydrogen concentration change in abiotic or pure CH_4 conditions.

Real-time Hydrogen Concentration Monitoring

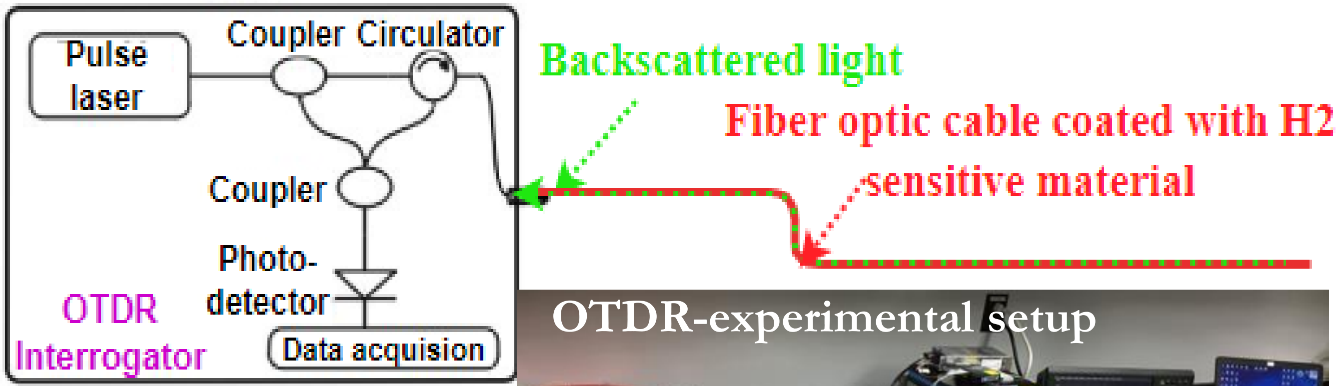


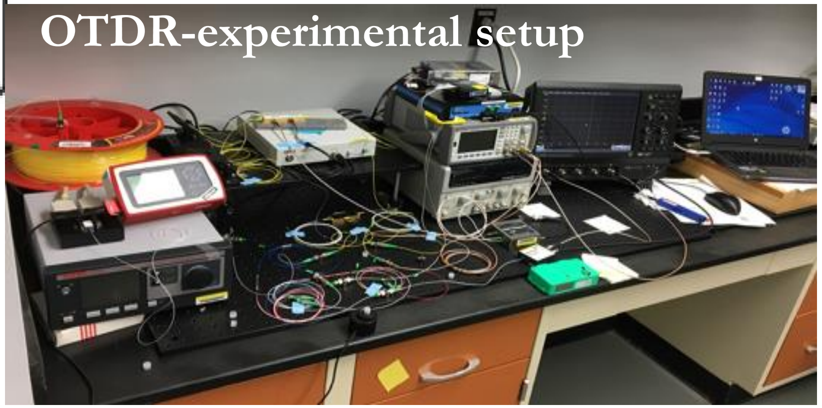
- ➢ The optical fiber H_2 sensor has demonstrated real-time H_2 sensing in simulated subsurface H_2 storage condition with microbes.
- ➢ According to the optical fiber hydrogen sensor, the hydrogen concentration seems to reach a steady state after 48 hours (decrease by 5-7%). The results here can benefit from duplicates to confirm repeatability.

Long-distance interrogation system for H_2 Pipeline sensing

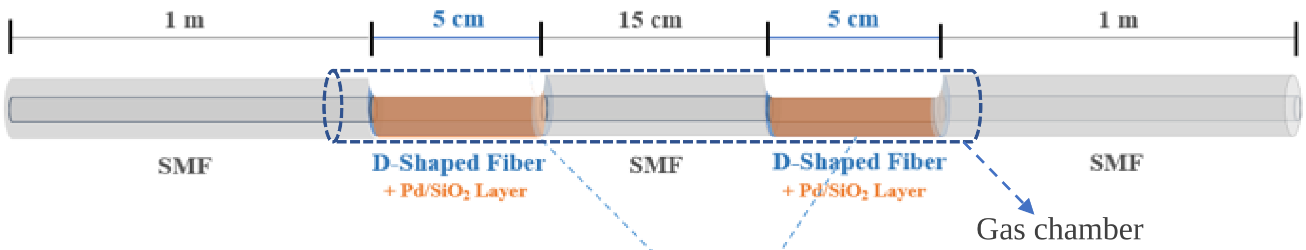
- Optical time domain reflectometry (OTDR) system has been developed for ultra-long distance (>50 km) hydrogen sensing.
- Currently working towards improving the sensitivity, lower concentration detection, and repeatability.

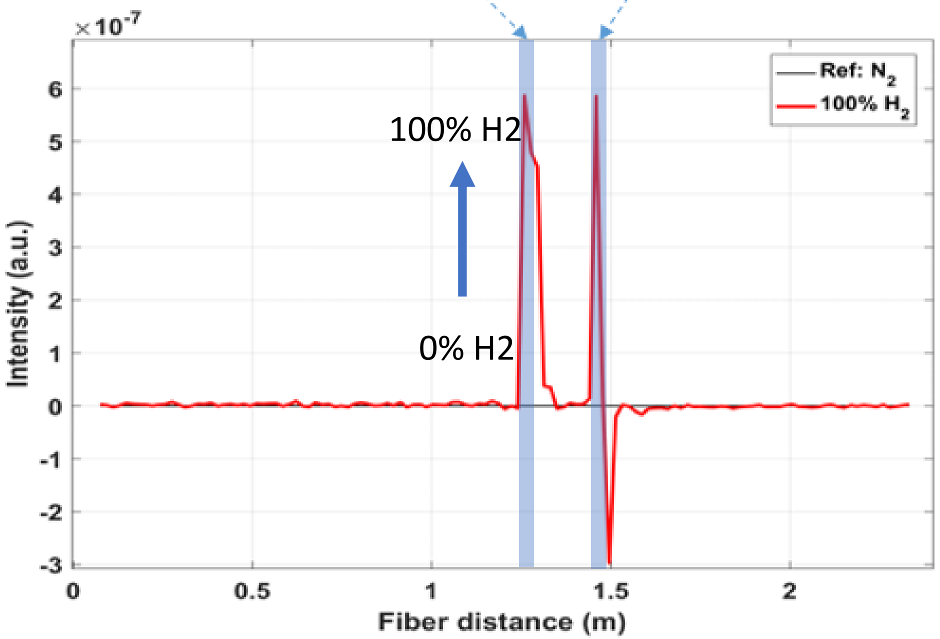
Schematic of distributed interrogation system





Distributed hydrogen sensor design example

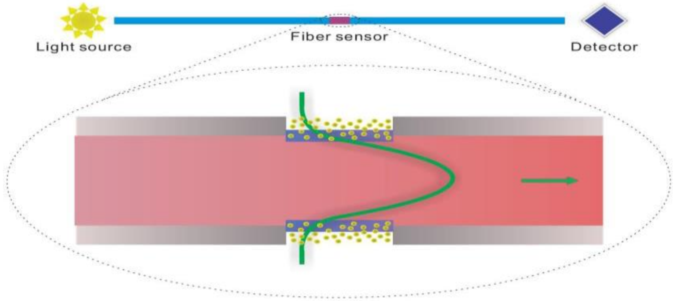




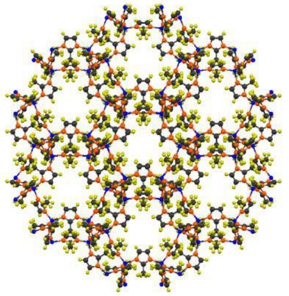
Measured Rayleigh backscattered signal for N_2 and 100% H_2

Optical Fiber Methane Sensing

Functional Sensing Layer Integrated Fiber Optic



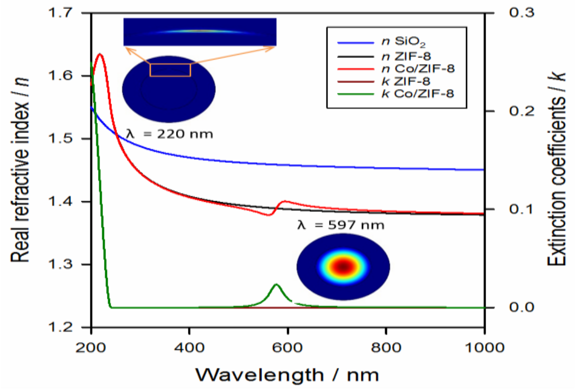
<u>Porous Metal Organic Framework (MOF)</u>



<u>Micro-porous Gas Permeable Polymers</u>

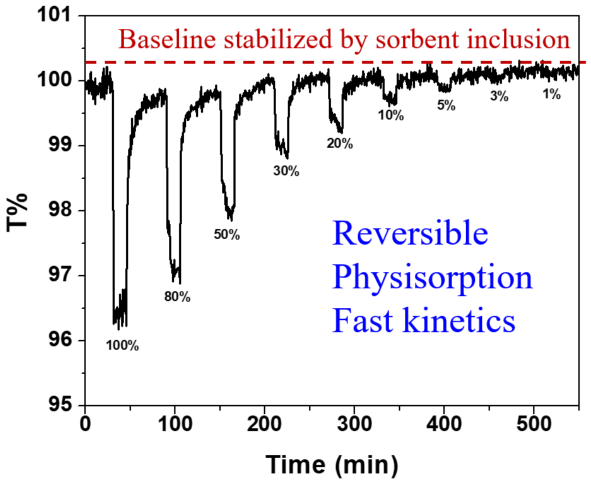
Evanescent Wave Absorption Based Sensors

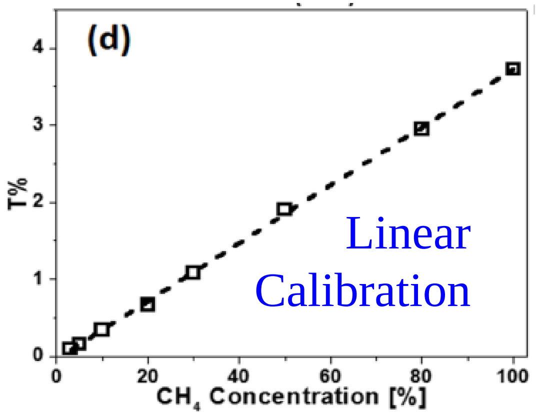
$$I_T(\lambda) = I_0 \exp[-\gamma\alpha(\lambda)CL]$$



Gas adsorption in the sensor coating causes $RI_{(coating)} > RI_{(fiber)}$, inducing optical power changes.

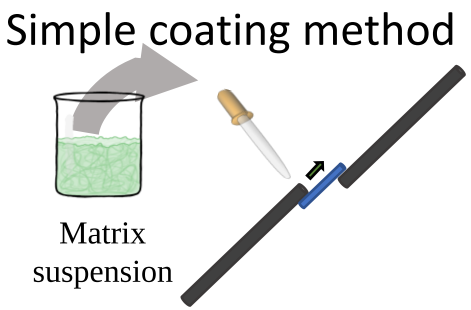
Ref: Kim et al, ACS Sensors, 2018, 3, 386-394.

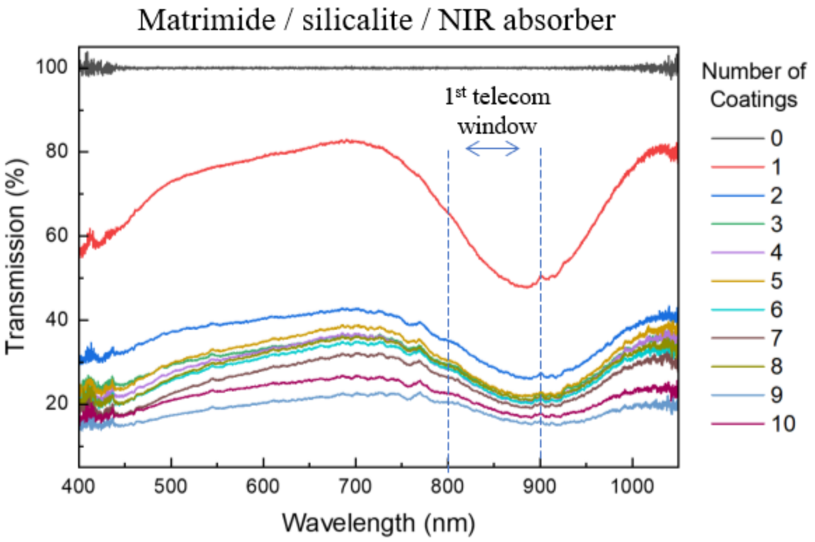


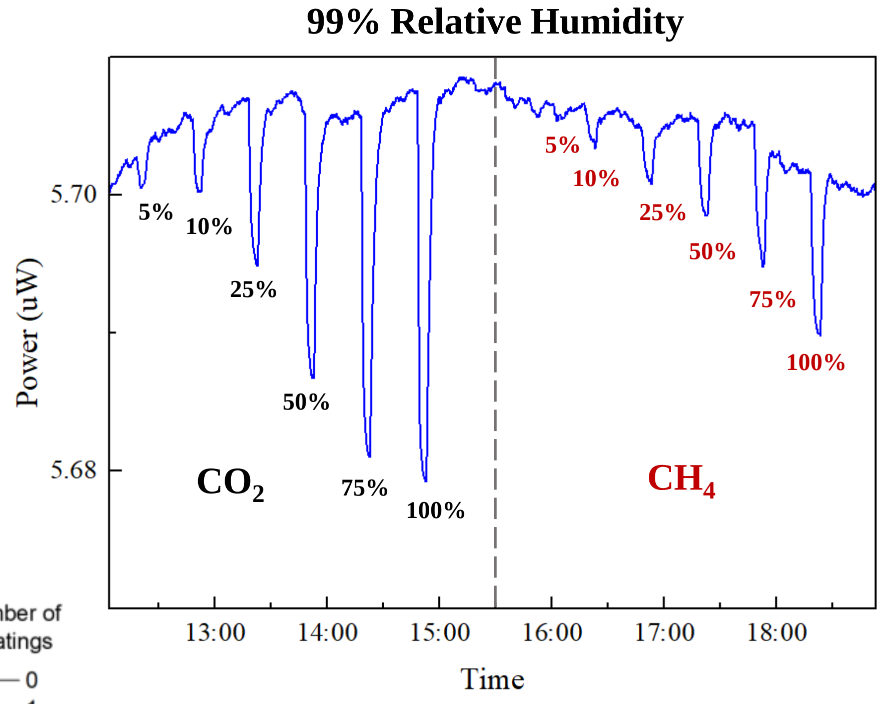


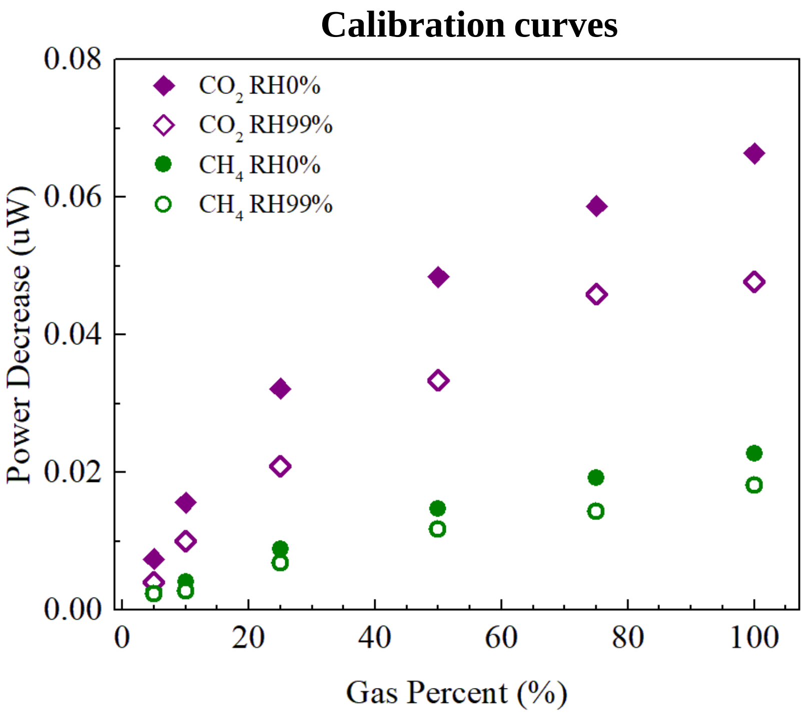
Light Intensity Based Methane Sensing Technology. Integration of Fiber Optic Sensors with Engineered Porous Sensing Layers by Design.

Optical fiber CH_4 sensor under humid conditions







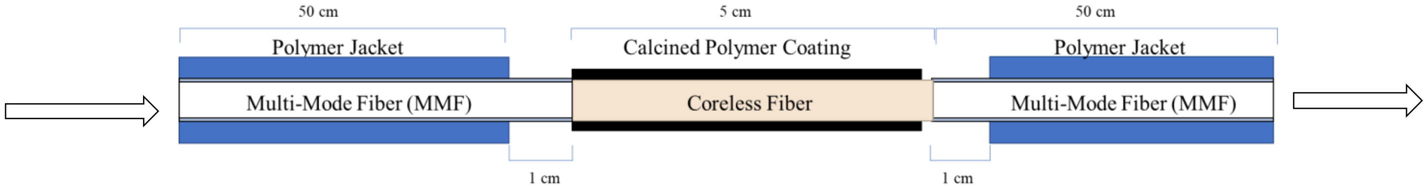


- Successful demonstration of optical fiber methane sensor in humid conditions at 99% relative humidity (RH)
- Tuned the wavelength to NIR range to be readily compatible with commonly used distributed OFS interrogators.
- Fast response time.
- Calibration curve of CO_2 and CH_4 from 5% to 100%.

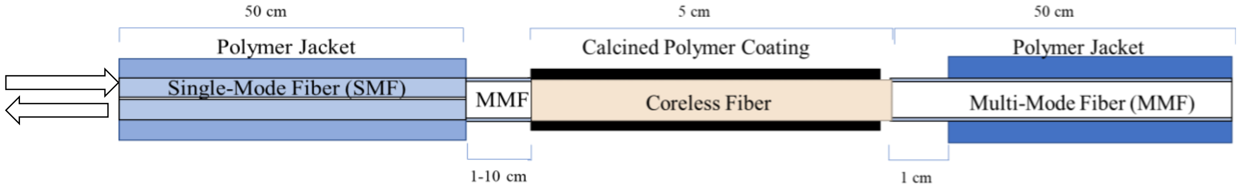
Optical Fiber pH Sensor

pH Sensing Measurements:

Transmission Based Sensor

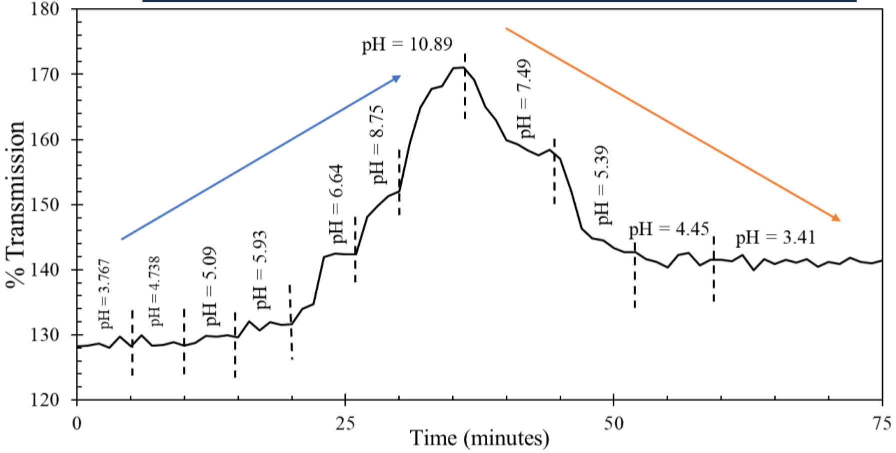


Optical Backscatter Reflectometry (OBR) Sensor

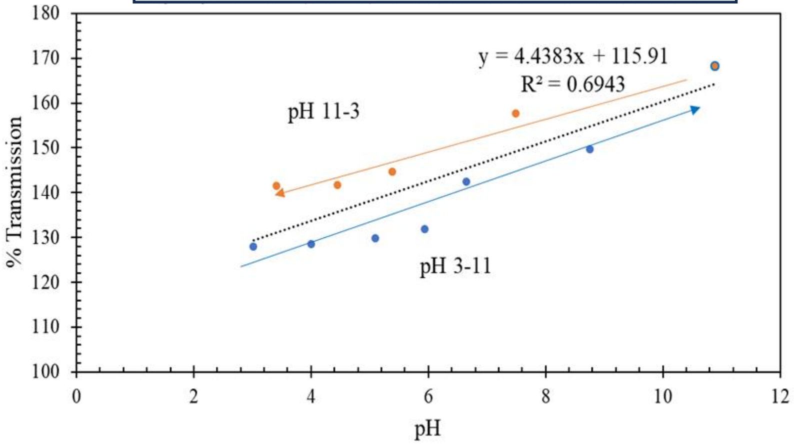


Transmission pH Sensing Results at 20 ^oC and 80 ^oC

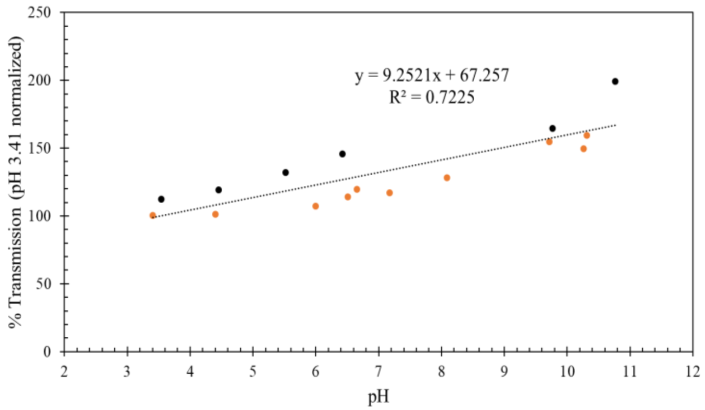
20 ^oC, dynamic pH sensing



20 ^oC pH calibration



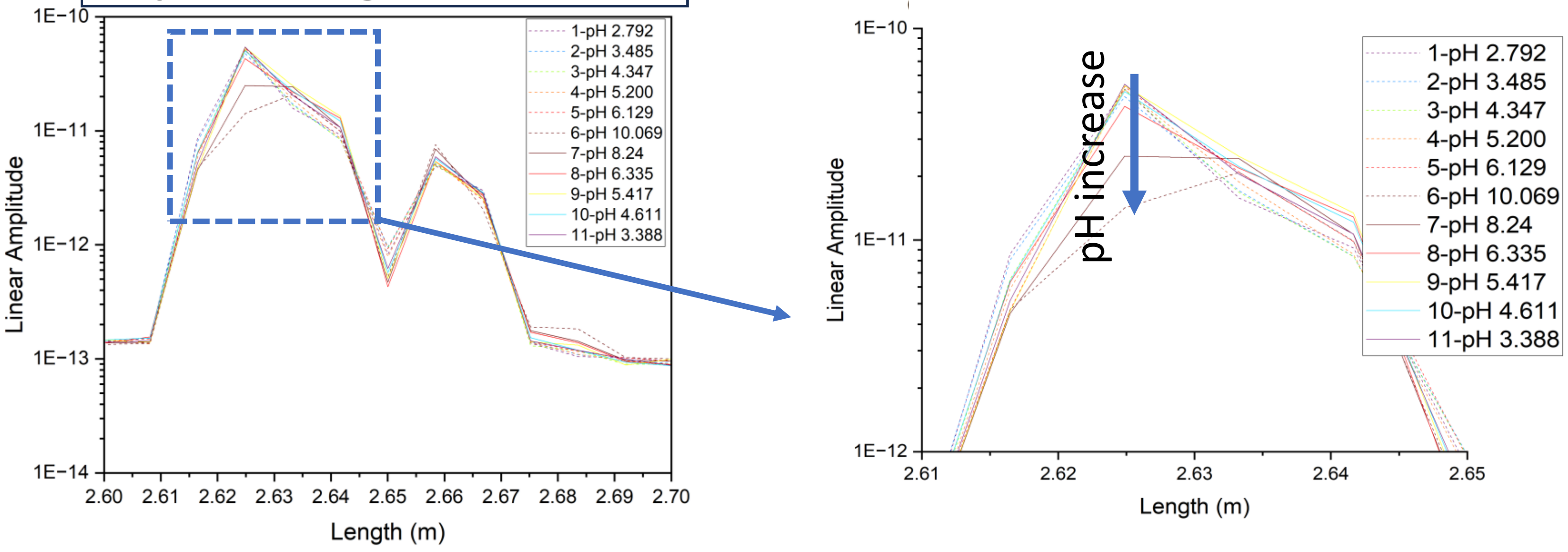
80 ^oC pH calibration

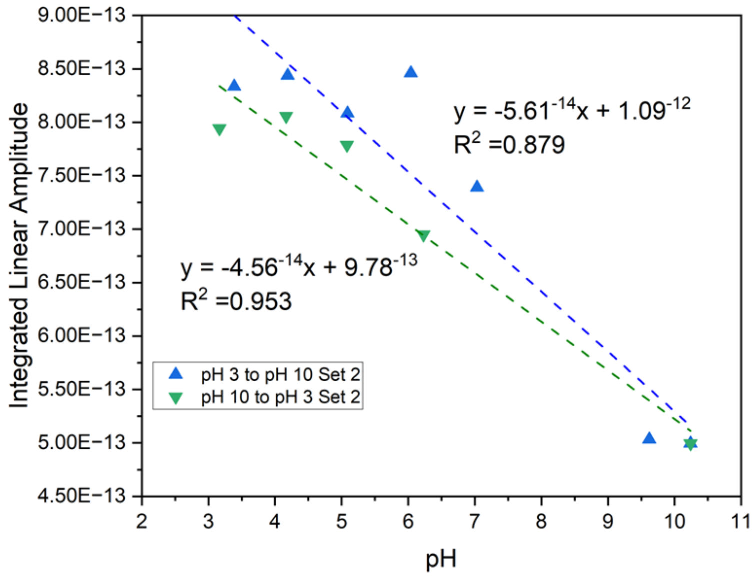


A new pH sensitive layer has showed reversible acid and base responses.

Distributed pH sensor results from OBR

pH sensing vs location





- Successfully demonstrated distributed pH sensing at 80 ^{o}C and obtained calibration.
- Backscattered light decreases as pH increases, opposite of transmitted light.

pH Sensor Performance Specifications	
Mechanism	Transmission/Backscattered light
pH Range	2-12
Temperature	20 to 80 $^{\circ}$C
Pressure	14.7 to 1000 psia
Compatibility	NaCl, Citrate, Carbonate, H_2, CH_4
Current TRL	5 to 6

Accomplishments and Future Plans

➢ Accomplishments

- Pd nanoparticle (NP) incorporated SiO_2 coated optical fiber H_2 sensor was demonstrated for a wide range of hydrogen sensing from 0.5% to 100 %. A new filter layer was developed to increase selectivity and mitigate humidity interference. Negligible cross-sensitivity from common cushion gas CO_2 or CH_4.
- The optical fiber H_2 sensor has demonstrated real-time H_2 sensing in simulated subsurface conditions with microbes (80 ^{o}C, 1000 psi), and detected hydrogen concentration change ***in situ and in real time***.
- Distributed hydrogen sensing can be achieved using optical time domain reflectometry (OTDR).
- Successful demonstration of optical fiber methane sensor in humid conditions at 99% relative humidity.
- Successfully demonstrated a new pH sensing material with reversible acid and alkaline pH sensing, and distributed pH sensing at 80 ^{o}C

➢ Future Plans for Sensor Development and Testing

	EY 21	EY 22	EY 23	EY 24	EY 25+
SHASTA: Subsurface Storage	Room temperature and ambient pressure	Humid, mixed gas conditions	High pressure, high temperature conditions	Sensor Packaging and Field Demo	
NGDHT: H_2 Transportation Monitoring		Hydrogen Sensing Materials Development	Low-level H_2 detection	Distributed Hydrogen Sensing	Prototype and Pilot-scale pipeline demonstration

Publications and Patents

Publications

- D. Kim, K.K. Bullard, A. Shumski, R. Wright, Optical Fiber Sensor with a Hydrophobic Filter Layer for Monitoring Hydrogen under Humid Conditions, ACS Sensors, manuscript draft completed, to be submitted in 2024.
- A presentation and a conference paper: "Calcined Polyethyleneimine Coated Optical Fibers for Distributed pH Monitoring at High Pressures and Temperatures" authored by Shumski, A., Diemler, N., Wright, R. will be presented at SPIE Defense + Commercial Sensing 2024 conference (April 21-25) **SPIE Defense + Commercial Sensing, 13044-20, 2024.**
- A presentation and a conference paper: "Pd Nanoparticles-Enabled Optical Fiber Hydrogen Sensor with a Hydrophobic Filter Layer for Humid Conditions" authored by Kim, D., Bullard, K., Diemler, N., Wright, R. was presented at SPIE Defense + Commercial Sensing 2023 conference (April 30-May 4) and accepted to *Proc. SPIE 12532*, **SPIE Defense + Commercial Sensing, 12532-3, 2023**.
- A presentation and a conference paper: "TiO_2-Coated Optical Fibers for Distributed pH Monitoring at High Pressures and Temperatures" authored by Shumski, A., Diemler, N., Wuenschell, J., Ohodnicki, P., Wright, R. was presented at SPIE Defense + Commercial Sensing 2023 conference (April 30-May 4) and accepted to *Proc. SPIE 12532*, **SPIE Defense + Commercial Sensing, 12532-22, 2023**.
- A presentation and a conference paper: "Physisorbent-Coated Fiber Optic Sensors for Near Ambient Leak Detection of CH_4 and CO_2" authored by Culp, J., Bullard, K., Kim, K., Wright, R. was presented at SPIE Defense + Commercial Sensing 2023 conference (April 30-May 4) and accepted to *Proc. SPIE 12532*, **SPIE Defense + Commercial Sensing, 12532-8, 2023**.
- Invited presentation "Gas Sensors for Energy Infrastructure Monitoring", Presenter: Ruishu Wright, **Pittcon 2023**, Philadelphia, PA, March 2023.
- A poster was given at **2022 AIChE Annual Meeting** (November 13-18, 2022), titled "Pd-nanoparticle enabled optical fiber hydrogen sensor for subsurface storage conditions" authored by D. Kim, N. Diemler, R. Wright, M.P. Buric, P.R. Ohodnicki.
- A presentation and a conference paper: "TiO_2 Coated Optical Fibers for Distributed Real-Time pH Monitoring in Wellbore Conditions" authored by Shumski, A., Diemler, N., Wright, R., Lu, F., Ohodnicki, P. and Su, Y. was presented at SPIE Defense + Commercial Sensing 2022 conference (April 3-7) and accepted to *Proc. SPIE 12105*, **SPIE Defense + Commercial Sensing** (SI22), **12105-21, 2022**.
- A presentation and a conference paper: "Metallic Film-Coated Optical Fiber Sensor for Corrosion Monitoring at High Pressures," authored by Wright, R.F., Diemler, N., Baltrus, J., Ohodnicki, P.R., Jr., Ziomek-Moroz, M., and Buric, M., was presented at **2022 AMPP Annual Conference + Expo**, March 6-10.

Patents

- U.S. Patent issued. 'Low-cost Fiber Optic Sensor Array for Simultaneous Detection of Multiple Parameters,' inventors: C. Sun, P. Lu, R. F. Wright, P.R. Ohodnicki, Jr., Patent Number: US11268984B2, issued on 2022-03-08.
- "Metal Oxides Enabled Fiber Optic pH Sensor for High temperature High pH Subsurface Environments" invented by F. Lu, R. Wright, P. Lu, P. R. Ohodnicki, U.S. Nonprovisional patent application filed, 2022-04-26. Application Number: 17729511.
- Hydrogen Monitoring under High Humidity Conditions Using the Optical Fiber Hydrogen Sensors Coated with a Hydrophobic Filter Layer, D. Kim, A. Shumski, R. Wright, ROI draft completed.

Acknowledgement

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