Advanced Sensors for Real-Time Monitoring of Natural Gas and Hydrogen Infrastructure

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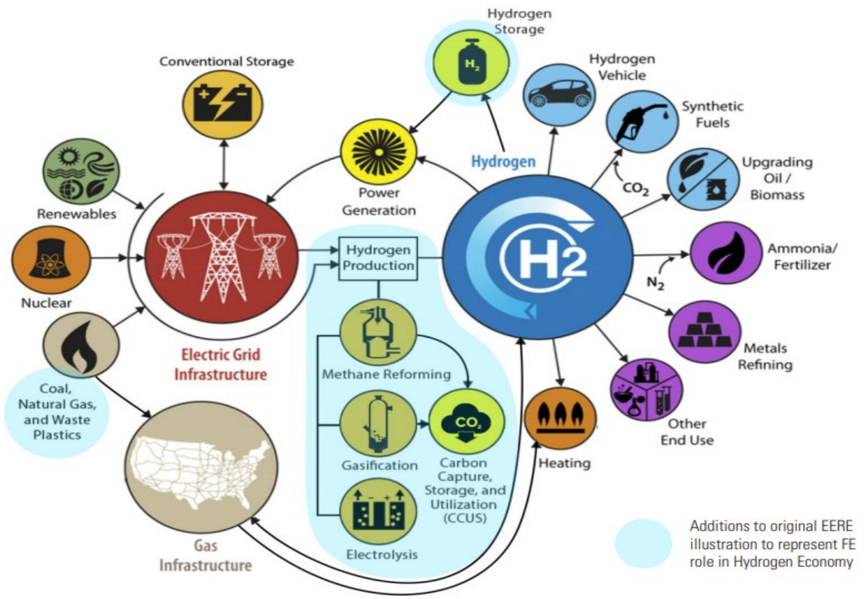
CH_4 Connections Conference 2023
Fort Collins, Colorado
October 4-5, 2023

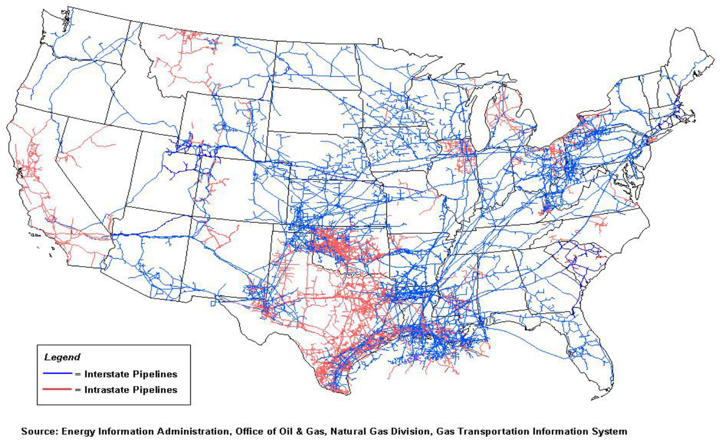
NATIONAL ENERGY TECHNOLOGY LABORATORY

U.S. DEPARTMENT OF ENERGY

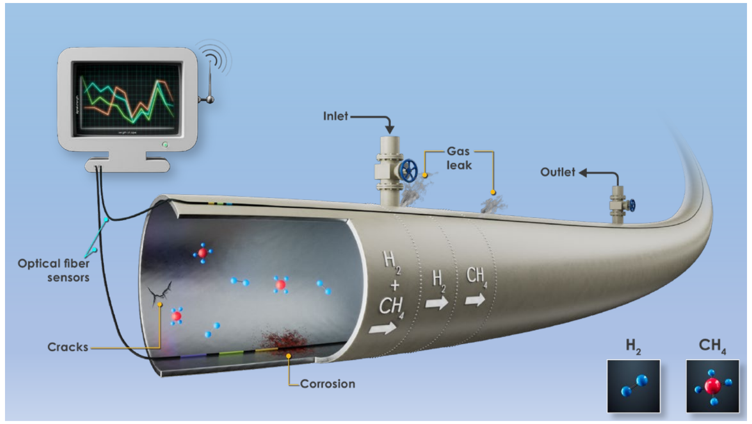
Repurpose of Natural Gas Infrastructure for Hydrogen Use

H2@Scale





HyBlend Pipeline

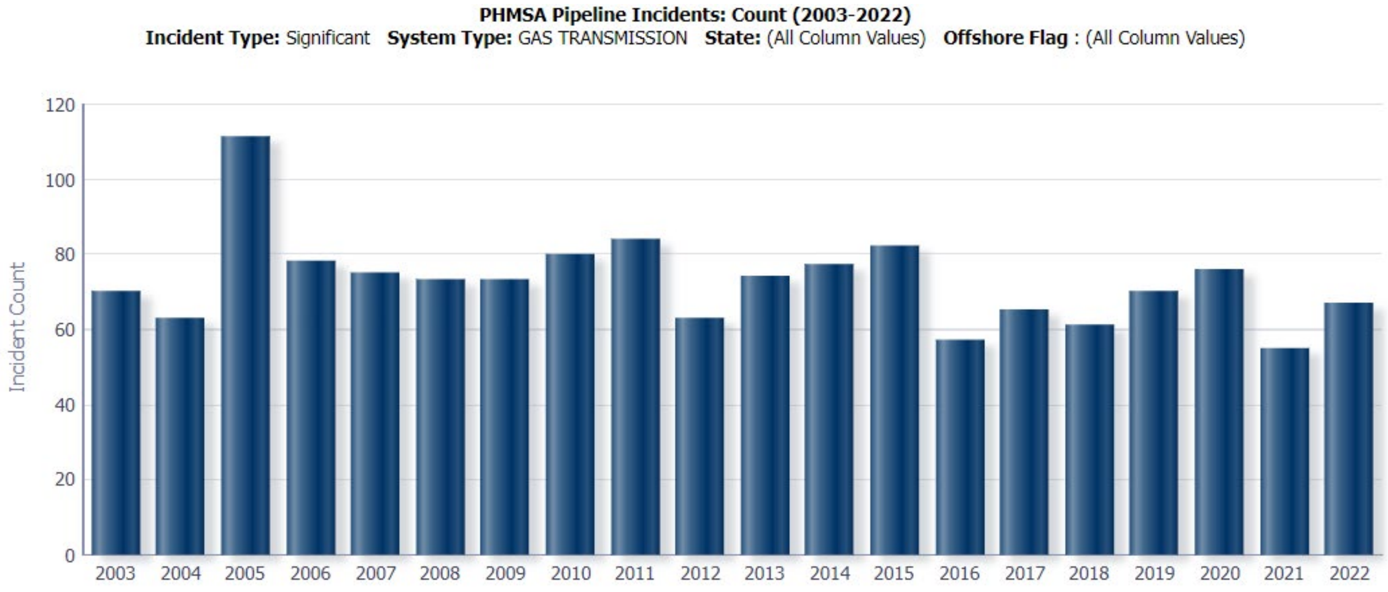


PHMSA Data:
NG Transmission Pipeline: **298,353 miles**
NG Distribution Pipeline: **2,296,214 miles**
Hydrogen Transmission Pipelines: **1,567 miles**
Hydrogen Distribution Main Pipelines: **1 mile**

- **NETL has established Natural Gas Infrastructure Program since 2016 to Quantify and Mitigate Midstream Methane Emission. NG decarbonization and Hydrogen Technology Program since 2022.**
- **Pipeline Sensors address pipeline reliability, public safety, operational efficiency, and flexibility.**

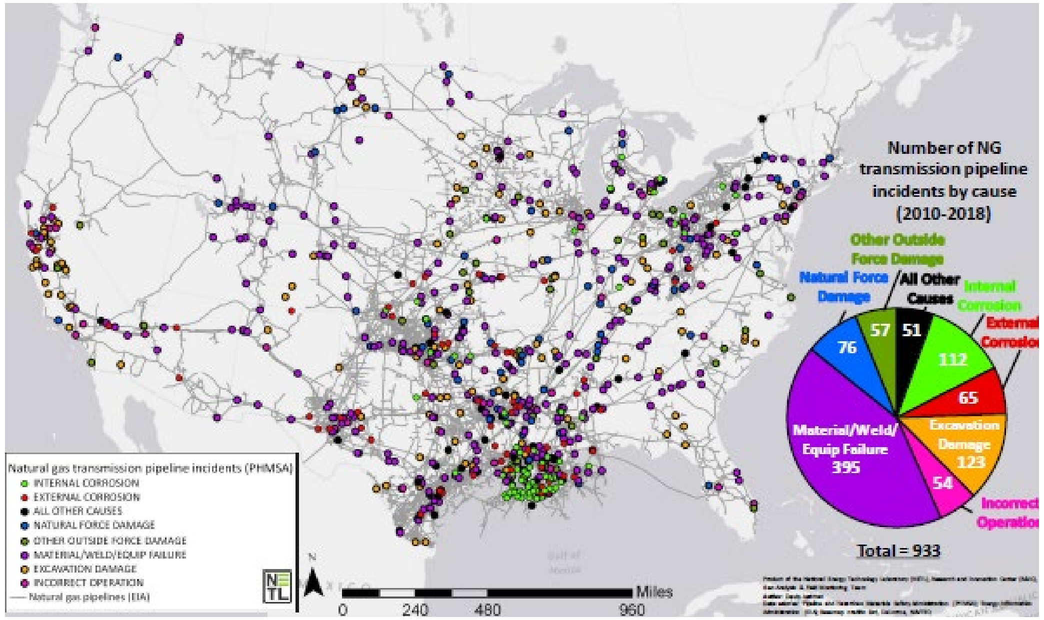
Safety is always #1 priority!

Significant Incidents of Gas transmission pipelines 2003-2022 (Source: PHMSA)



20-year average: 73 incidents / year; cost $143 M / year

Natural Gas Transmission Pipeline Incidents (2010-2018)



Ref: Justman, Rose & Bauer, NETL, 2017. Data analyzed from U.S. DOT PHMSA incident data

Real-time and predictive monitoring can reduce risks and improve safety.

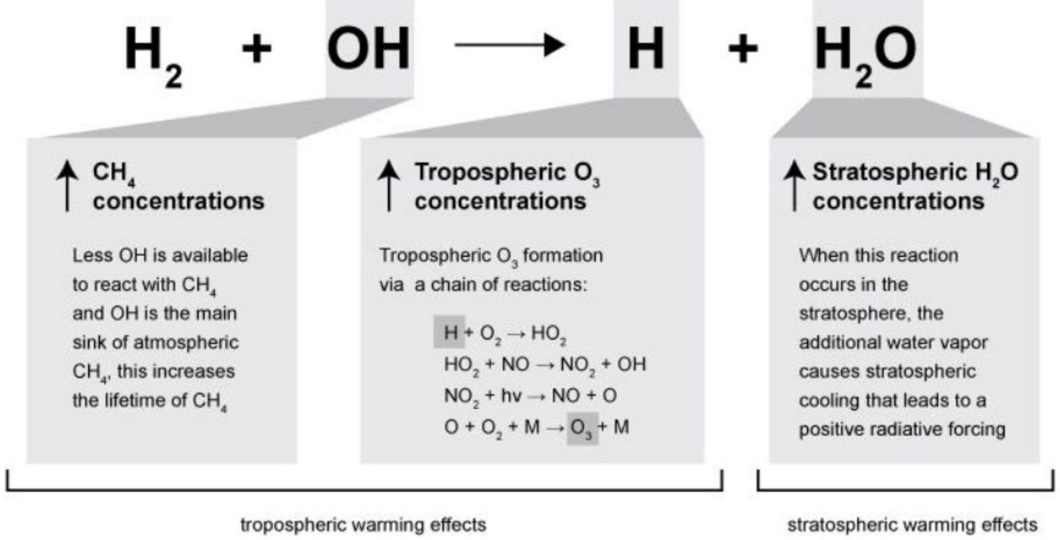
Environmental Impact

CH_4 is > 25 times more potent than CO_2

- Natural gas systems emitted 181.4 MMT CO_2 Eq. (6,478 kt CH_4) of CH_4 in 2021. Methane emissions from the transmission and storage segment accounted for approximately 25 percent of emissions from natural gas systems. (EPA)
- <u>**Silver lining**</u>: CH_4 life time is ~ 12 years while CO_2 effect can last centuries, meaning CH_4 emission mitigation could have a quicker effect on slowing down global warming.

Current CH_4 in atmosphere: **1922 ppb**; H_2 in atmosphere: **530 ppb**

Hydrogen as an indirect greenhouse gas



Reference: Ilissa B. Ocko, Steven P. Hamburg, 'Climate consequences of hydrogen leakage', https://doi.org/10.5194/acp-2022-91

"Green H_2 can mitigate atmospheric methane if hydrogen losses throughout the value chain are below 9 ± 3%. Blue H_2 can reduce methane emissions only if methane losses are below 1%. "

Highly sensitive monitoring of CH_4 and H_2 at ppb level are important to evaluate global warming effects and GHG impact modeling.

Source: 1. Global Monitoring Laboratory.
2. Bertagni, et al 2022, Nature Communications

State of the Art of Methane Sensors

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Methane Sensor Types	Working Mechanisms	Advantages	Disadvantages
Catalytic pellistors	Burn the target gas and the generated heat produces a change in the semiconductor resistance, w	Robust performance Easy operation Straightforward to install, calibrate and use	Require O_2 to operate. Heated. Poor selectivity
Optical sensors	Detect changes in light waves that result from an interaction of the analyte with the receptor part.	Non-destructive method; Immune to electromagnetic interference; Operate without oxygen.	High cost; High power consumption; Lack of significance and distinctiveness of methane optical absorption region.
Calorimetric sensors	Measure the heat produced from a reaction and correlate the value to the reactant concentration.	Low cost; Simplistic design; Portable; Easy to manufacture; Good selectivity for methane; Can operate in harsh environmental conditions.	Low detection accuracy; Susceptible to cracking, catalyst poisoning and oversaturation; High power consumption; Short lifespan; Require high temperature.
Pyroelectric sensors	Convert thermal energy into electrical energy based on the phenomenon of pyroelectricity.	Non-destructive; Operate without oxygen; Good sensitivity and responsivity; Wide measuring range; Operate at room temperature.	High cost; High power consumption; Immobile; Difficult to manufacture.
Semiconducting metal oxide sensors	Absorption of gas on the surface of a metal oxide changes its conductivity, which is then quantified to obtain the gas concentration.	Low cost; Lightweight and robust; Long lifespan; Resistant to poisoning.	Poor selectivity; Small and high operational temperature range; Slow recovery rate; Significant additive dependency; Affected by temperature; Susceptible to degradation; Sensitive to changes in humidity
Electrochemical sensors	Measure the target gas concentration by oxidizing or reducing the gas at an electrode and measuring the resulting current.	AE-based: Low cost. IL-based: Non-hazardous materials; High boiling points and low volatility; Good selectivity for methane; Can detect small leaks. SE-based: No leakage; Safe; Robust; Good selectivity for methane; Can detect small leaks.	AE-based: Susceptible to leakage and evaporation; Hazardous materials; Slow response time. IL-based: Susceptible to leakage; Slow response time. SE-based: Require high temperature; Unable to detect low gas concentrations; Susceptible to degradation or loss of electrolyte.

Ref: Aldhafeeri, et al *Inventions* 5, no. 3: 28;
T. Hong et al. Trends in Analytical Chemistry 125 (2020) 115820

State of the Art of Hydrogen Sensors

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

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

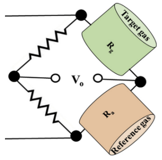
H_2 Sensors

Catalytic

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

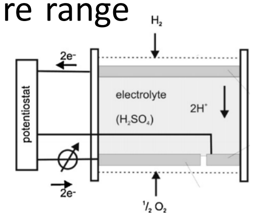
Thermal

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

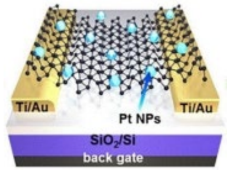


Resistive

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

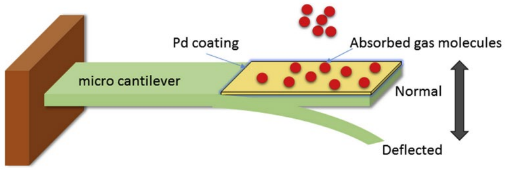
Work Function

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



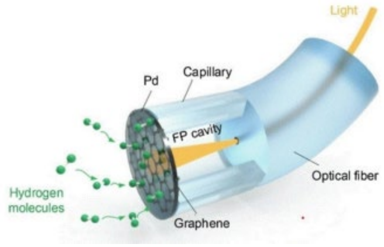
Mechanical

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

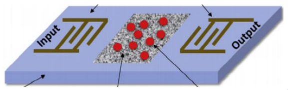


Optical

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



Acoustic

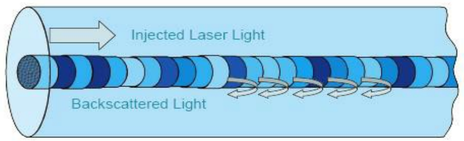


frequency, wave velocity, time: **P**
high sensitivity, fast response :**A**
interference from humidity, drift :**D**

NETL Advanced Sensor Technologies

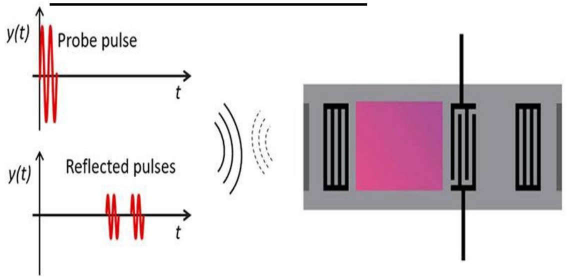
Distributed Optical Fiber Sensor

Imperfections in fiber lead to Rayleigh backscatter:

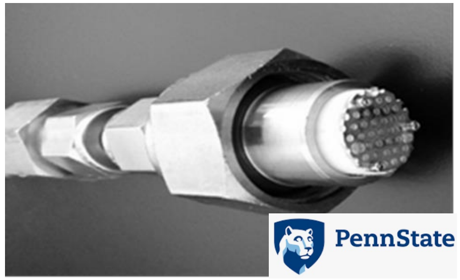


Rayleigh backscatter forms a permanent spatial "fingerprint" along the length of the fiber.

Passive Wireless Surface Acoustic Sensor



Advanced Electrochemical Sensor

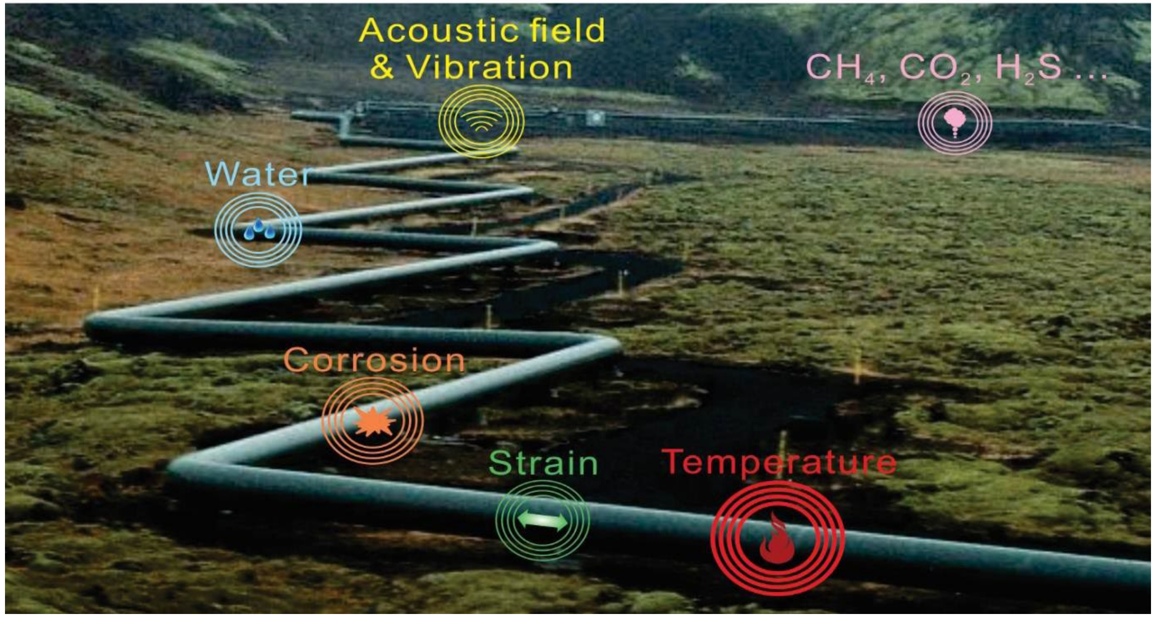


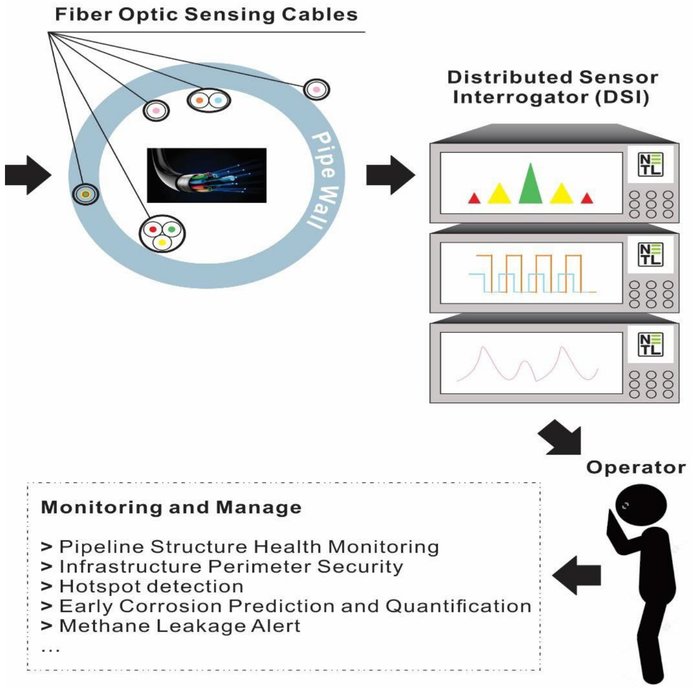
	Geospatial Attributes	Cost	Targeted Function	TRL
Distributed Optical Fiber Sensors	Linear Sensor Adjustable Distance and Resolution	Cost Per Sensor "Node" Low	Temperature, Strain, Gas Chemistry (CH_4, CO_2, H_2O, H_2, etc.) Early Corrosion/pH Detection	5-6
Passive Wireless SAW Sensors	Point Sensor	Low	Temperature, Strain, Gas Chemistry (CH_4, CO_2, H_2O, H_2, etc.) Early Corrosion/pH Detection	4-5
Advanced Electrochemical Sensor	Point Sensor	Moderate	Water Content, Corrosion Rate, T, Pitting Corrosion	5-6

Three Synergistic Sensor Platforms with Complementary Cost, Performance, and Geospatial Characteristics are being Developed with an Emphasis on Corrosion & Gas Monitoring.

Distributed Optical Fiber Sensor Network for Pipelines

Pipeline Integrated with Distributed Optical Fiber >100 km





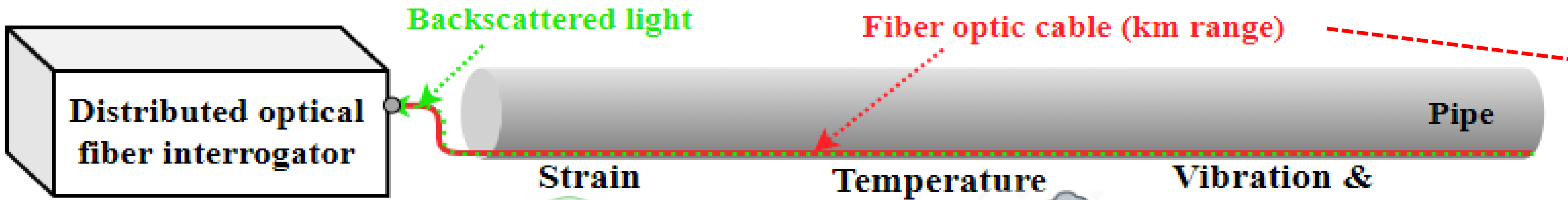
- Optimize Interrogation System (Range, Resolution, Cost)
- Early **Corrosion** On-Set Detection → **Predictive Signatures**
- **Methane or hydrogen Leak** Detection & In-Pipe Gas Composition Monitoring → **Direct Signatures**

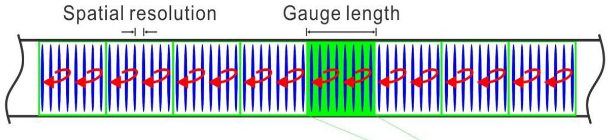
Multi-Parameter, Distributed Optical Fiber Sensor Platform to Enable Reliable and Resilient Pipelines.

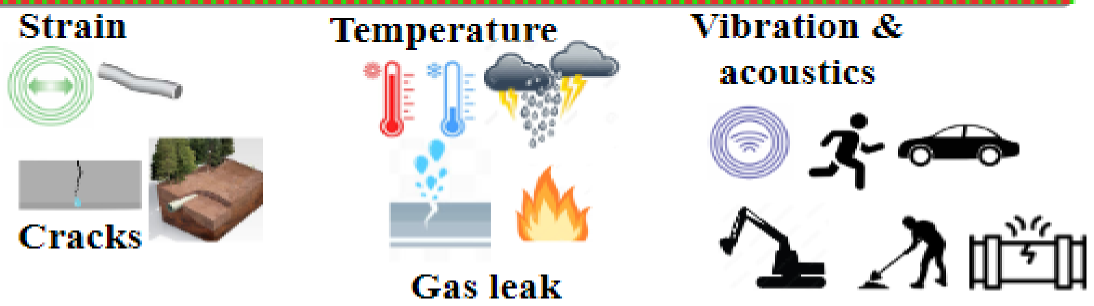
>100 km Interrogation, <1 to 5 m Spatial Resolution

Distributed Optical Fiber Interrogator Development

Pipeline integrity monitoring based on various distributed fiber sensor systems





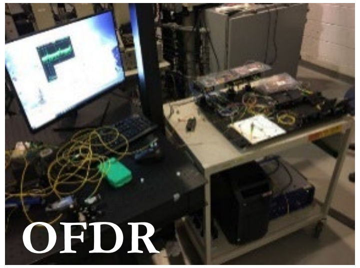


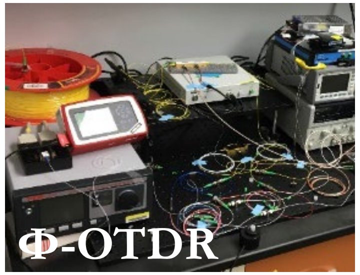
Sensing information with location:

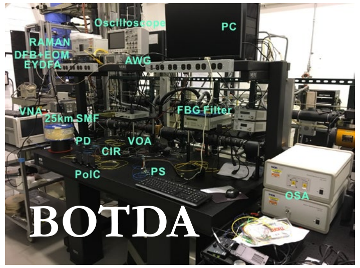
- Leak detection
- Flow monitoring
- Developing cracks/deformation
- Temperature distribution along pipe
- Seismic events/intrusion detection
- Remote monitoring

In-House NETL Distributed Optical Fiber Sensor Interrogators

Technology	Sensing range	Spatial resolution	Measurement time	Target parameter
Rayleigh phase-OTDR	Kilometers	Meters	Seconds	Acoustic/vibrations
Brillouin- OTDA	Tens of kilometer	Centimeter to meter	Minutes	Temperature and strain
Rayleigh OFDR	Meter to kilometer	Millimeter to centimeter	Seconds	Temperature and strain

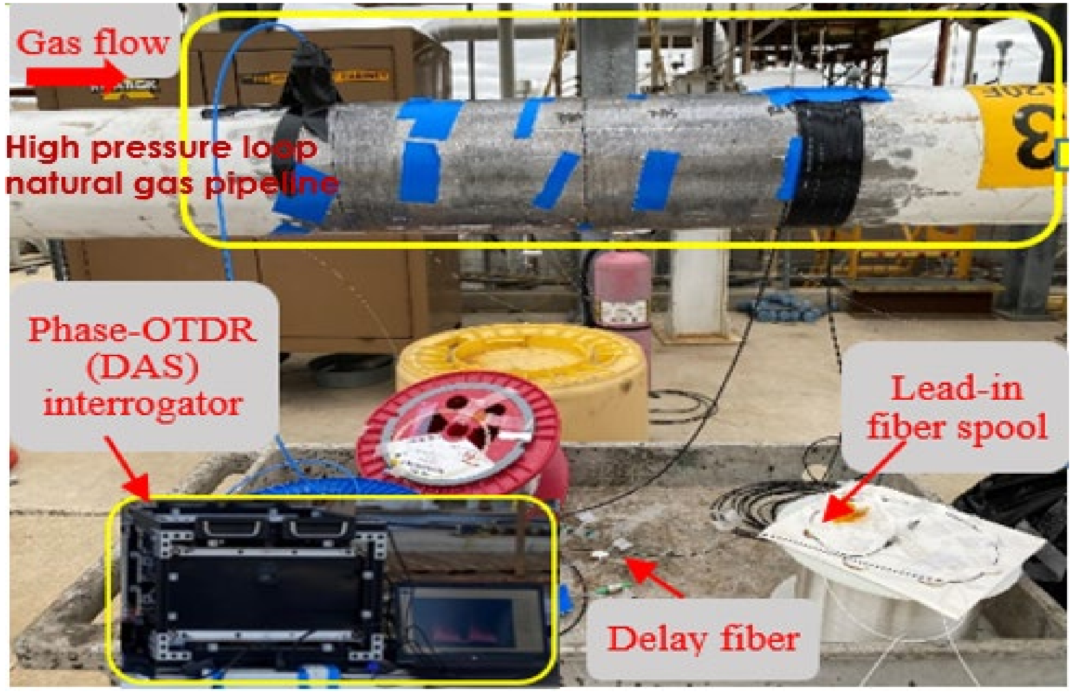






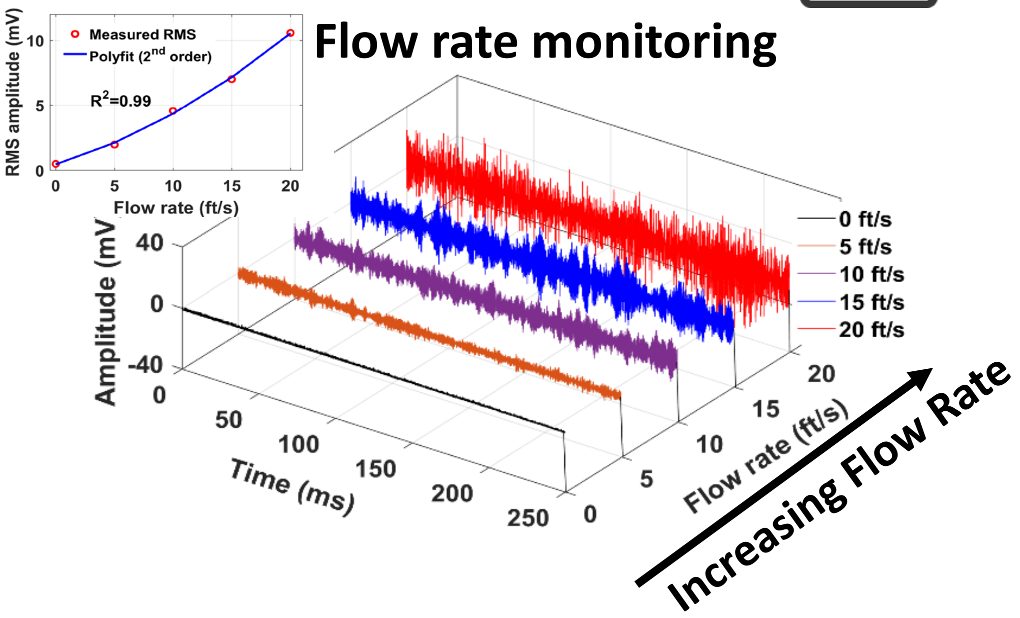
Multiple distributed optical fiber sensing platforms have been developed to enable structural health monitoring of pipeline and other infrastructure.

Distributed Acoustic Sensing Pilot-scale Field Demonstration



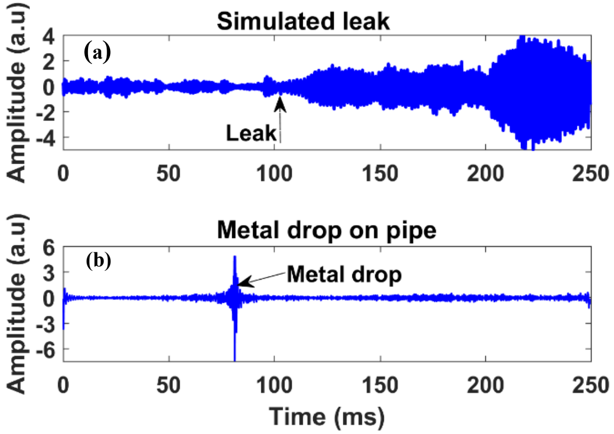
- Flow rate monitoring
- Leak detection
- Third party intrusion detection

Flow rate monitoring



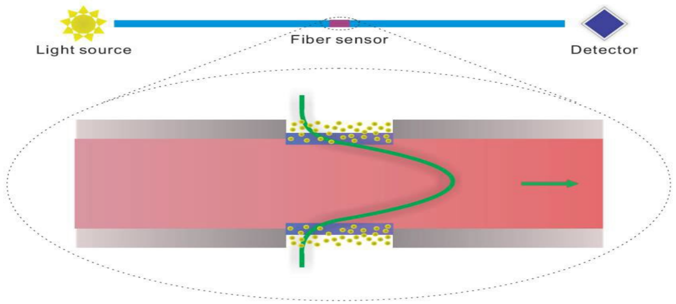
Gas leak detection

Metal nut drop onto the pipe

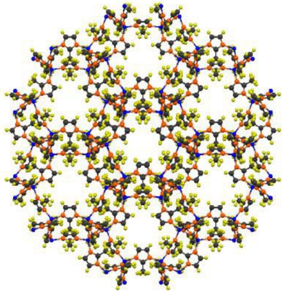


Optical Fiber Methane Sensing

Functional Sensing Layer Integrated Fiber Optic



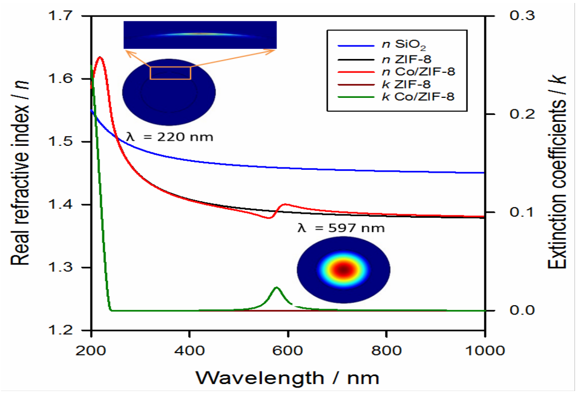
Porous Metal Organic Framework (MOF)



Micro-porous Gas Permeable Polymers

Evanescent Wave Absorption Based Sensors

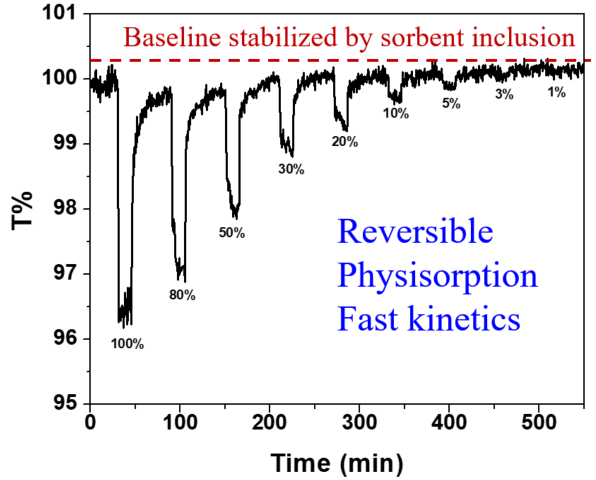
$$I_T(\lambda) = I_0 \exp[-\gamma\alpha(\lambda)CL]$$

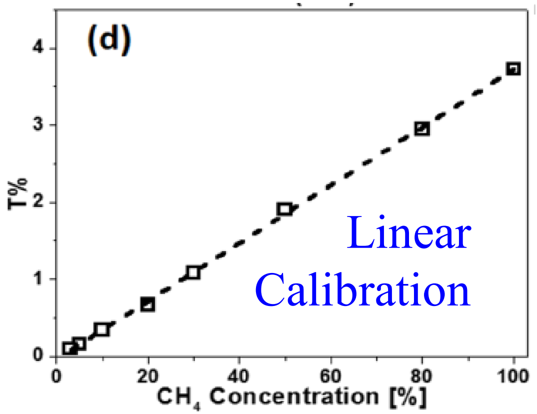


Gas adsorption in the sensor coating causes $RI_{(coating)} > RI_{(fiber)}$, inducing optical power changes.

Kim et. al, *ACS Sens*. 2018, 3, 386–394

CH_4 Detection Limit: < 5% in N_2





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

Optical Fiber Hydrogen Sensor

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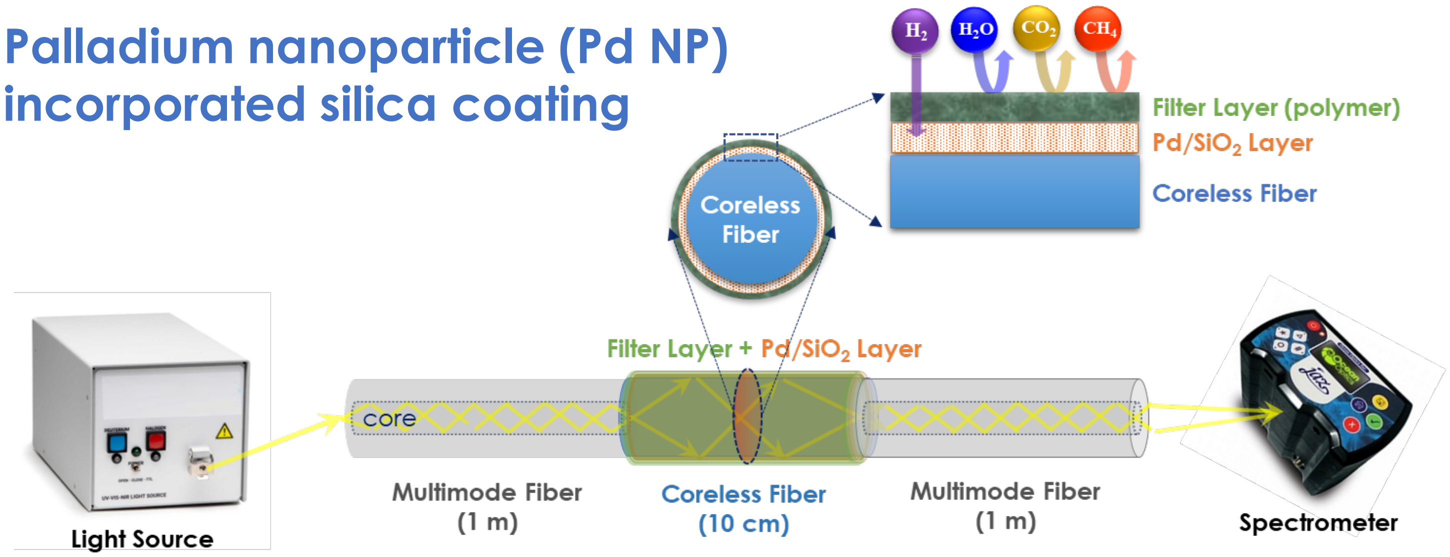
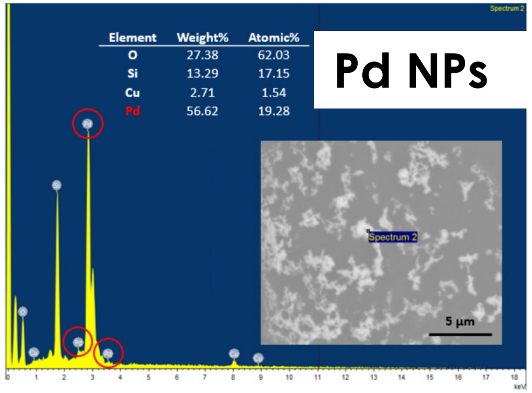
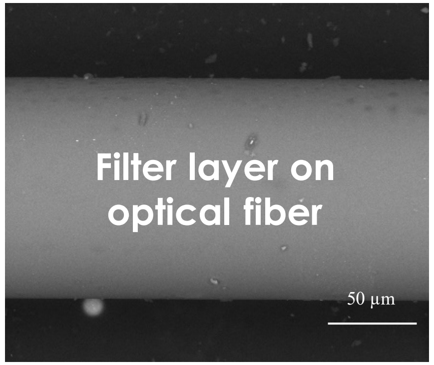
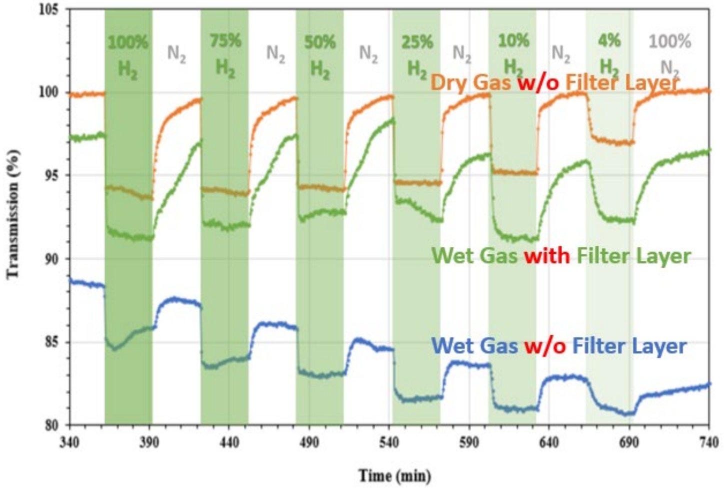
Palladium nanoparticle (Pd NP) incorporated silica coating



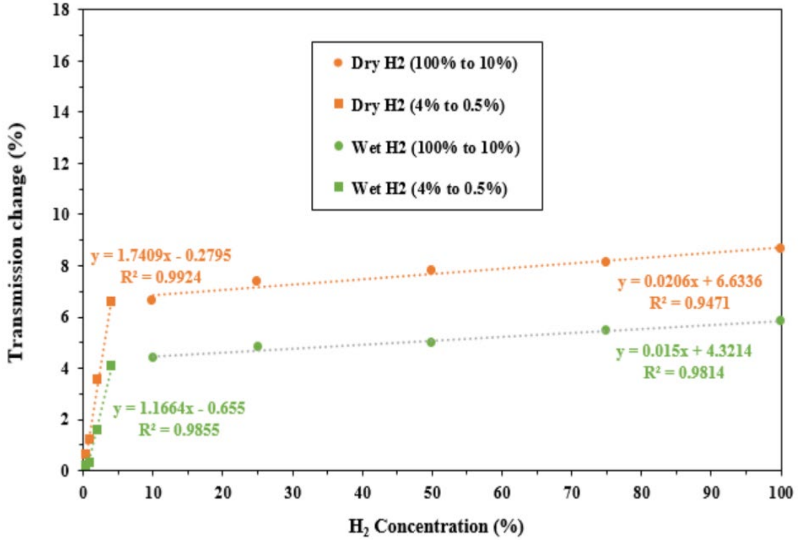




H2 sensing in 99% relative humidity with a newly developed filter layer.



H2 sensing calibration plot



- Pd nanoparticle (NP) incorporated SiO_2 coated optical fiber H_2 sensor was developed.
- H2 sensing calibration plots under humidity conditions for a wide range of 0.5% to 100%.

Passive Wireless Surface Acoustic Wave (SAW) Sensors

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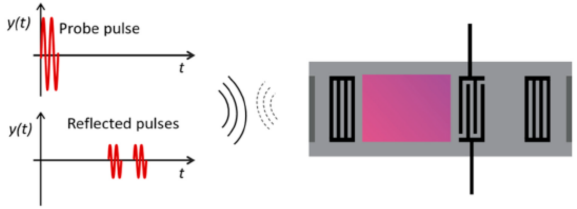
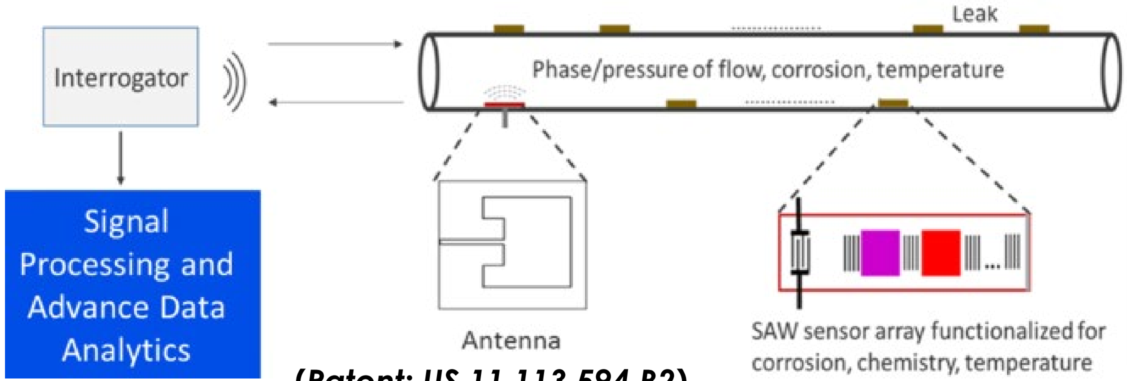
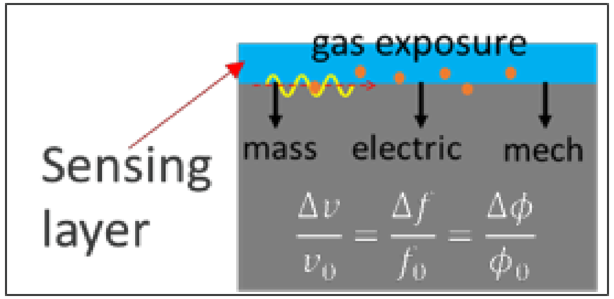
- **Passive, Wireless, Matured Devices**
- **Sensitive, Cheap Point Sensors**
- **Possible for Multi-Parameter Operation** (Temperature, Pressure, Strain, Chemical Species, Corrosion etc.)



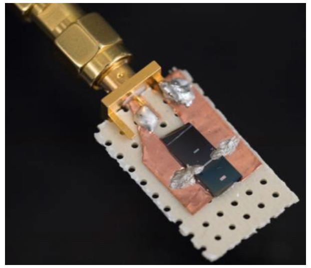


(Patent: US 11,113,594 B2)

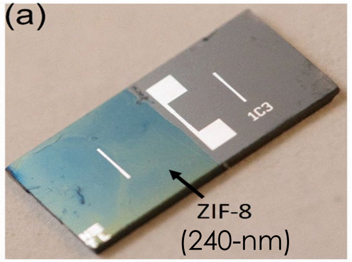
Sensing Principle



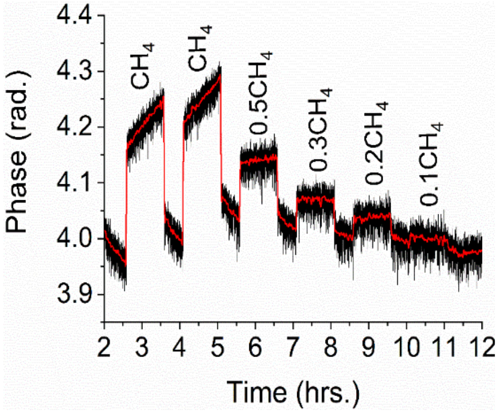
SAW sensor



SAW sensor with sensitive coating



CH_4 sensing results

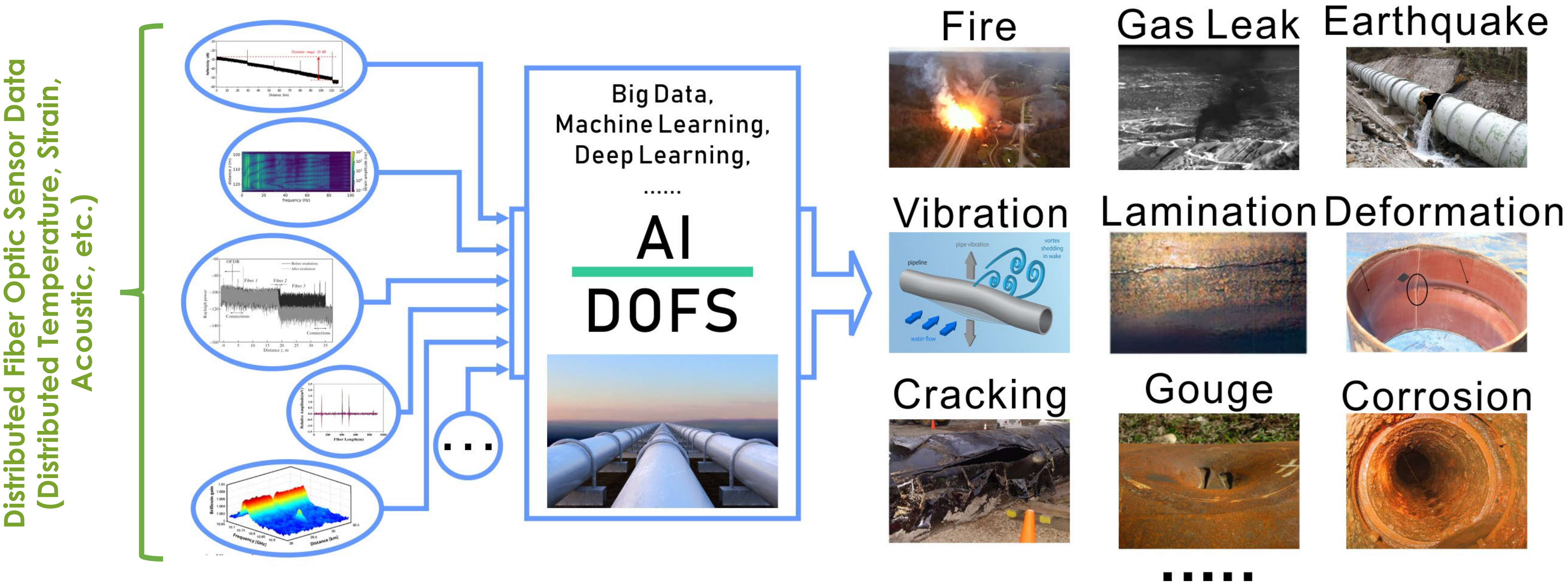


(Devkota et al., IEEE *Sensors Journal, 9740 – 9747 (2020)*

Low-cost passive wireless methane sensors have been developed at NETL.

Artificial Intelligence-enhanced Distributed Sensor Network

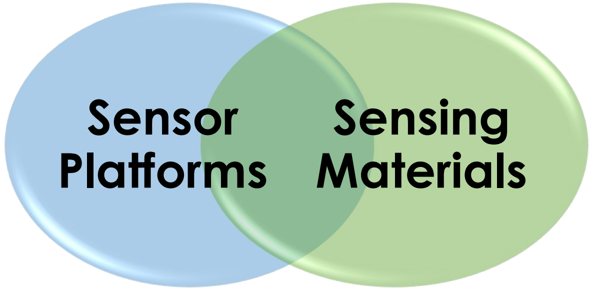
Fiber Optic Based Distributed OFS Technology Integrated with Advanced Analytics Including Pattern and Feature Recognition Can Convert Large Data Sets to Actionable Information.



Sensor Materials for Critical Infrastructure and **Extreme Environments**

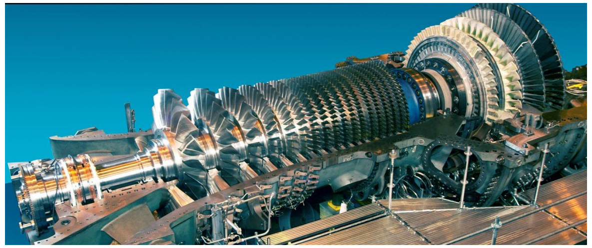
Advanced Sensors for Energy Efficiency, Safety, Resilience, and Sustainability

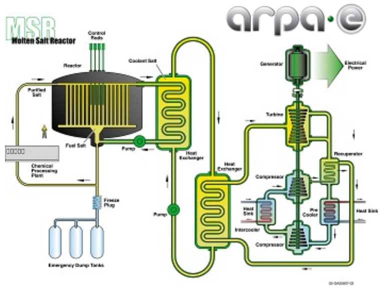
- ✓ Monitor systems and conditions
- ✓ Improve performance & efficiency
- ✓ Enhance reliability & safety
- ➢ Temp, acoustics, chemical, gas, corrosion
- ➢ Composite nano-materials, thin films & fiber optics, sensor devices development



GENERATION

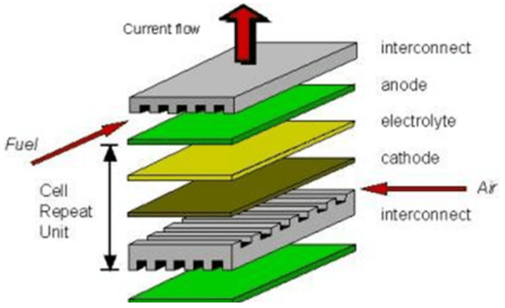
Turbines: Real-time fuel composition and combustion temperature for improved service life and efficiency





Nuclear: Core monitoring and molten salt temperatures for reactor fuel efficiency & reactor safety

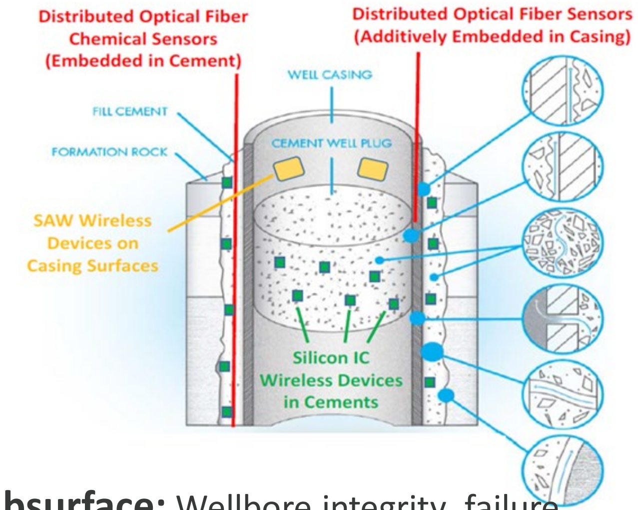
SOFCs: Fuel concentration & temperature gradients for improved lifetime and efficiency



ENERGY DELIVERY & STORAGE

Pipelines: Monitor corrosion, gas leaks, T, acoustics to predict/prevent failures. NG, H_2, CO_2

Grid: Transformer, powerline failure prediction, fault detection, state awareness



Subsurface: Wellbore integrity, failure prediction, leak detection. Geologic storage of CO_2, H_2/NG, or abandoned wells.

Summary

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- For safety and global warming impact evaluation, it is critical to monitor low-concentration CH_4 and H_2 leaks in real time to mitigate greenhouse gas emissions and ensure safe operations using the flammable gases.
- Multiple complementary sensor technologies developed at NETL can support gas leak monitoring, leveraging the advantages of ***optical, electrochemical, and microwave / wireless sensor platforms***, to build an in-situ, multi-parameter, distributed, and cost-effective sensor network.
- ***A wide range of sensing materials*** are developed to achieve high sensitivity, selectivity, and fast response, including MOF, polymers, and nanocomposites.
- Predictive and early detection of structural and equipment failures can inform timely maintenance and mitigate risks and gas emissions.
- Artificial intelligence-enhanced sensor network with ubiquitously embedded sensors will ultimately achieve desired visibility across the energy infrastructure.

Acknowledgement and Disclaimer

Acknowledgement

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Backup slide

Performance Metrics of Commercially Available H_2 Sensors

NATIONAL ENERGY TECHNOLOGY LABORATORY

Sensor type	Principle/Device	Accuracy /% of indication	Response time (t90)/s	Power consumption/ mW	Gas environment	Lifetime /years	High detection limit/vol%	Low detection limit	*Ref.
Catalytic	Pellistor	<±5	<30	1000	-20~70 °C, 5-95% RH, 70~130kPa	5	4	**2000 ppm***	Henriquez 2021
Thermal Conductivity	Calorimetric	±0.2	<10	<500	0-50 °C, 0~95% RH, 80-120 kPa	5	100	**200 ppm***	Park, 2014
Electrochemical	Amperometric	≤±4	<90	2-700	-20~55 °C, 5~95 RH, 80-110 kPa	2	4	**10 ppm***	Korotcenkov, 2009
Resistance based	Semiconducting metal-oxide	±10-30	<20	<800	-20~70 °C, 10~95% RH, 80-120 kPa	>2	2	**10 ppb***	Yadav 2020
	Metallic resistor	≤±5	<15	>25	0~45 °C, 0~95% RH, up to 700 kPa	<10	100	**500 ppm***	Kondalkar 2021
Work function based	Capacitor	≤±7	<60	4000	-20~40 °C, 0~95% RH, 80~120 kPa	10	5	**1000 ppm***	Sahoo 2021
	MOS field effect transistor	≤±7	<2	700	-40~110 °C, 5-95% RH, 70~130 kPa	10	4.4	**100 ppm***	Sahoo 2021
Optical	Optrode	±0.1	<60	1000	-15~50 °C, 0~95% RH, 75~175 kPa	>2	100	**500 ppm***	Liu 2019
Acoustic	Surface acoustic wave	n/a	n/a	n/a	Room temp., 55% RH*	n/a	2*	**100 ppm***	Wang 2012

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Source: Hubert et al. Hydrogen Sensors – A Review, Sensors and Actuators B 157 (2011) 329-352
*(**Note: *found in peer review research paper (Ref.)**)*