Real-time Sensor Technologies for H₂ Subsurface Storage and Transportation Monitoring

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Enabling large-scale H$_2$ storage and transportation

- 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.

(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)
Real-time Sensors for H₂ Subsurface Storage and Transportation Monitoring

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

Natural Gas Decarbonization and Hydrogen Technology FWP (NGDHT)

- Spatially Distributed
- Real-time In-situ
- >100 km range

Project Period: 04/2021-04/2024
Project Objectives

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

**Impact on Subsurface Hydrogen Storage**

- Determine microbiological H₂ 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)

Catalytic

- P: temperature, resistance
  - A: robust, stable, wide operating temperature range
  - D: requires O₂, 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

Optical

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

Mechanical

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

Acoustic

- P: frequency, wave velocity, time
  - A: high sensitivity, fast response
  - D: interference from humidity, drift
Approach: Optical Fiber Sensors

Sensing Principle: Evanescent Wave Sensors

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 H₂, CH₄, 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.
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$_2$O conditions.

<table>
<thead>
<tr>
<th>Application</th>
<th>Depth</th>
<th>Average Temperature</th>
<th>Pressure</th>
<th>pH Range</th>
<th>Dissolved Solids</th>
<th>Common Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$ and H$_2$/CH$_4$ Blend Storage</td>
<td>200-2000 m</td>
<td>25-100 °C</td>
<td>5-30 MPa</td>
<td>4-9.5</td>
<td>10,000-70,000 mg/L</td>
<td>Sulfides, CO$_2$/Carbonate, Cl$^-$, Na$^+$, K$^+$, H$_3$O$^+$, Ca$^{2+}$, Mg$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, Fe$^{II/III}$</td>
</tr>
</tbody>
</table>

(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.**
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.
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 H₂ sensor has no cross-sensitivity to CO₂ and CH₄

- In order to guarantee a minimum reservoir pressure, the reservoir is filled with a cushion gas such as CO₂, N₂, or possibly NG.
- Under 99% relative humidity, the optical fiber H₂ sensor with the filter layer has shown negligible effects from CO₂ or CH₄.
Sensor Tests in Simulated HPHT wellbore conditions with Microbial Samples

Subsurface Sensor Development Reactor (SSDR)

**SSDR capability:**

**Automation** with LabView: Batch and Flow-through Modes;

**High-Temperature High-Pressure** (HTHP): up to 450 °C, 4500 psi;

**Multi-phase:** aqueous, gas, supercritical;

**Gas:** H₂, CO₂, CH₄, N₂, Air, H₂S.

T: 80 °C; P: ~850-1000 psi.

<table>
<thead>
<tr>
<th>Type</th>
<th>Liquid Phase</th>
<th>Gas Phase</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>DI</td>
<td>CH₄ or 80/20 CH₄/H₂</td>
<td>3</td>
</tr>
<tr>
<td>Abiotic: CH₄</td>
<td>Filtered PDR</td>
<td>CH₄</td>
<td>1,3,7</td>
</tr>
<tr>
<td>Biotic: CH₄</td>
<td>Unfiltered PDR</td>
<td>CH₄</td>
<td>1,3,7</td>
</tr>
<tr>
<td>Abiotic: H₂+ CH₄</td>
<td>Filtered PDR</td>
<td>80/20 CH₄/H₂</td>
<td>1,3,7</td>
</tr>
<tr>
<td>Biotic: H₂+ CH₄</td>
<td>Unfiltered PDR</td>
<td>80/20 CH₄/H₂</td>
<td>1,3,7</td>
</tr>
</tbody>
</table>

PDR = Playa Del Rey wellbore fluid provided by SoCalGas
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% CH4 biotic conditions.
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 CH₄ conditions.
The optical fiber H₂ sensor has demonstrated real-time H₂ sensing in simulated subsurface H₂ 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.
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

Measured Rayleigh backscattered signal for N\textsubscript{2} and 100\% H\textsubscript{2}
Light Intensity Based Methane Sensing Technology. Integration of Fiber Optic Sensors with Engineered Porous Sensing Layers by Design.

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.
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 °C and 80 °C

20 °C, dynamic pH sensing

20 °C pH calibration

80 °C pH calibration

A new pH sensitive layer has showed reversible acid and base responses.
Distributed pH sensor results from OBR

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

### pH Sensor Performance Specifications

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Transmission/Backscattered light</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH Range</td>
<td>2-12</td>
</tr>
<tr>
<td>Temperature</td>
<td>20 to 80 °C</td>
</tr>
<tr>
<td>Pressure</td>
<td>14.7 to 1000 psia</td>
</tr>
<tr>
<td>Compatibility</td>
<td>NaCl, Citrate, Carbonate, H₂, CH₄</td>
</tr>
<tr>
<td>Current TRL</td>
<td>5 to 6</td>
</tr>
</tbody>
</table>

**pH sensing vs location**

**Graphical Representation**
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 °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 °C.

Future Plans for Sensor Development and Testing

- **SHASTA**: Subsurface Storage
  - EY 21: Room temperature and ambient pressure
  - EY 22: Humid, mixed gas conditions
  - EY 23: High pressure, high temperature conditions
  - EY 24: Sensor Packaging and Field Demo
  - EY 25+: Prototype and Pilot-scale pipeline demonstration

- **NGDHT**: H$_2$ Transportation Monitoring
  - Hydrogen Sensing Materials Development
  - Low-level H$_2$ detection
  - Distributed Hydrogen Sensing

Accomplishments and Future Plans
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 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: “Metallic Film-Coated Optical Fiber Sensor for Corrosion Monitoring at High Pressures,” authored by Wright, R.F., Diemler, N., Baltruš, J., Ohodnicki, P.R., Jr., Ziomek-Moroz, M., and Buric, M., was presented at 2022 AMPP Annual Conference + Expo, March 6-10.

Patents

- 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

Program Manager: Evan Frye (DOE, FECM)
Technology Manager: Bill Fincham (NETL)
Technical Portfolio Leads: SHASTA: Angela Goodman (NETL);
NGDHT: Dan Haynes, Ruishu Wright (NETL)

Disclaimer

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