Intrinsic Fiber Optic Chemical Sensors for Subsurface Detection of CO_2

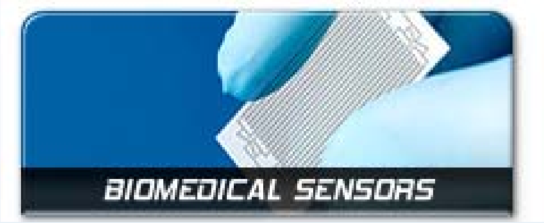
Intelligent Optical Systems, Inc.

Jesús Delgado Alonso, PhD
Robert A. Lieberman, PhD

DOE Technical Monitor: Barbara Carney

Intelligent Optical Systems, Inc. (IOS)

- Founded in April, 1998
- Focus areas:
  - Physical, chemical, and biomedical optical and electronic sensors
  - Advanced light sources and detectors
- >$3.5M in equipment
- 11,500 sq. ft. facility in Torrance, CA
- Several spin-off companies with >$22M in private funding



Intrinsic Fiber Optic Chemical Sensors for Subsurface Detection of CO_2

- Technology
- History and Objectives
- Project Phases
- Progress
- Planned Work
- Conclusions

Problem/Opportunity

Reliable and cost-effective monitoring is important to making gas sequestration safe

Desirable analytical systems characteristics:

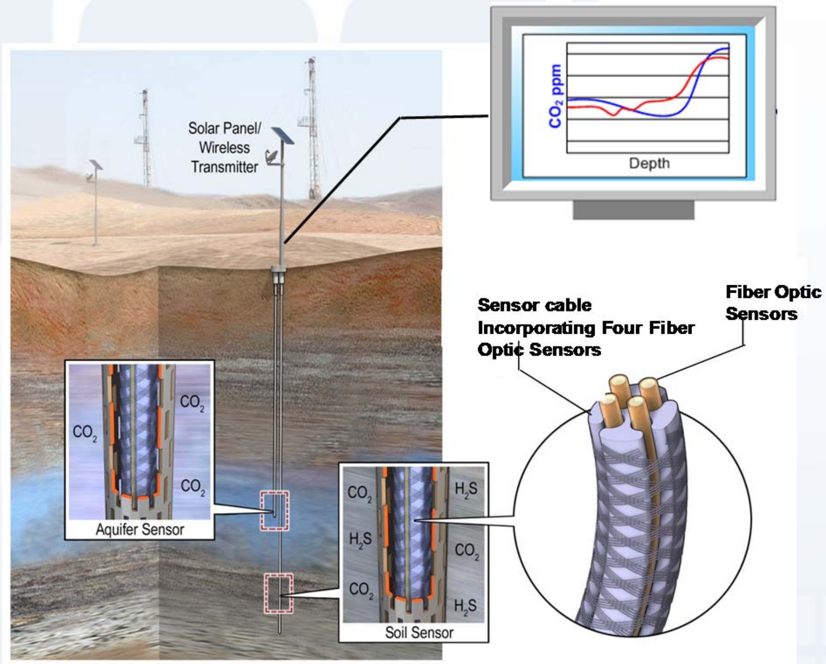
- Provide Reliable Information
- Monitor continuously
- Cover large areas
- Operate for years with little or no maintenance
- Cost effective
- Differentiate between CO_2 variations due to natural processes and those due to leaks of exogenous gas

Technology

Distributed intrinsic fiber optic sensors for the direct detection of carbon dioxide.

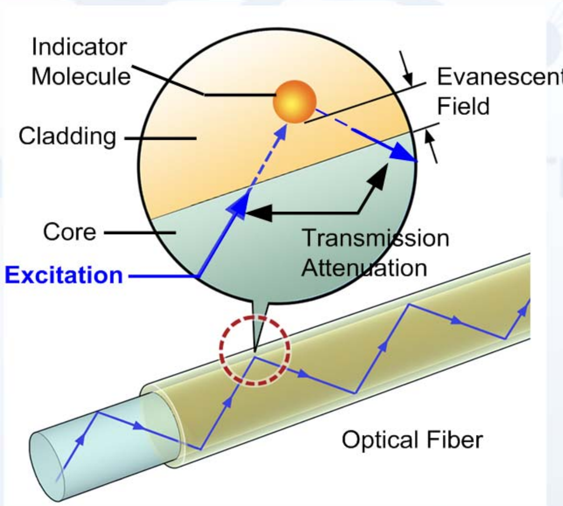
Unique characteristics:

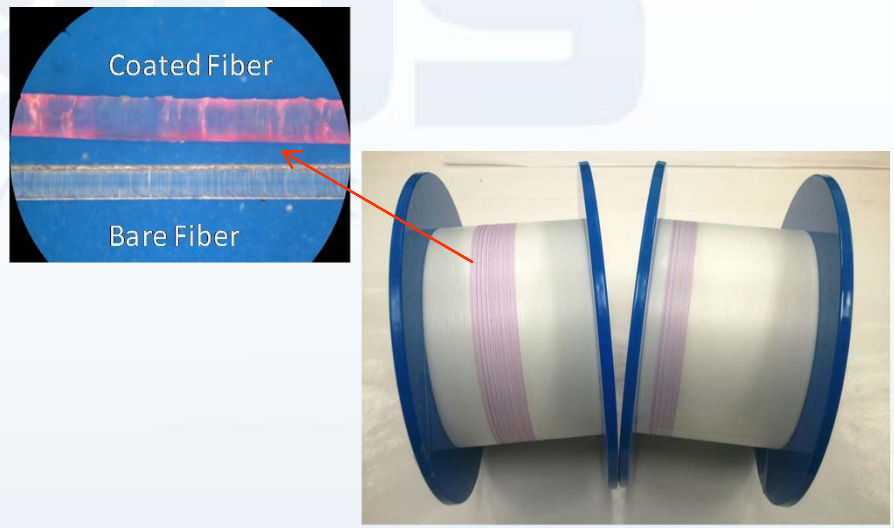
- Direct measurement of CO_2
- The entire length of an optical fiber is a sensor
- Sensors are capable of monitoring CO_2 in water and in gas phase
- A single cable may include CO_2, pH, salinity, and temperature sensors.



Technology

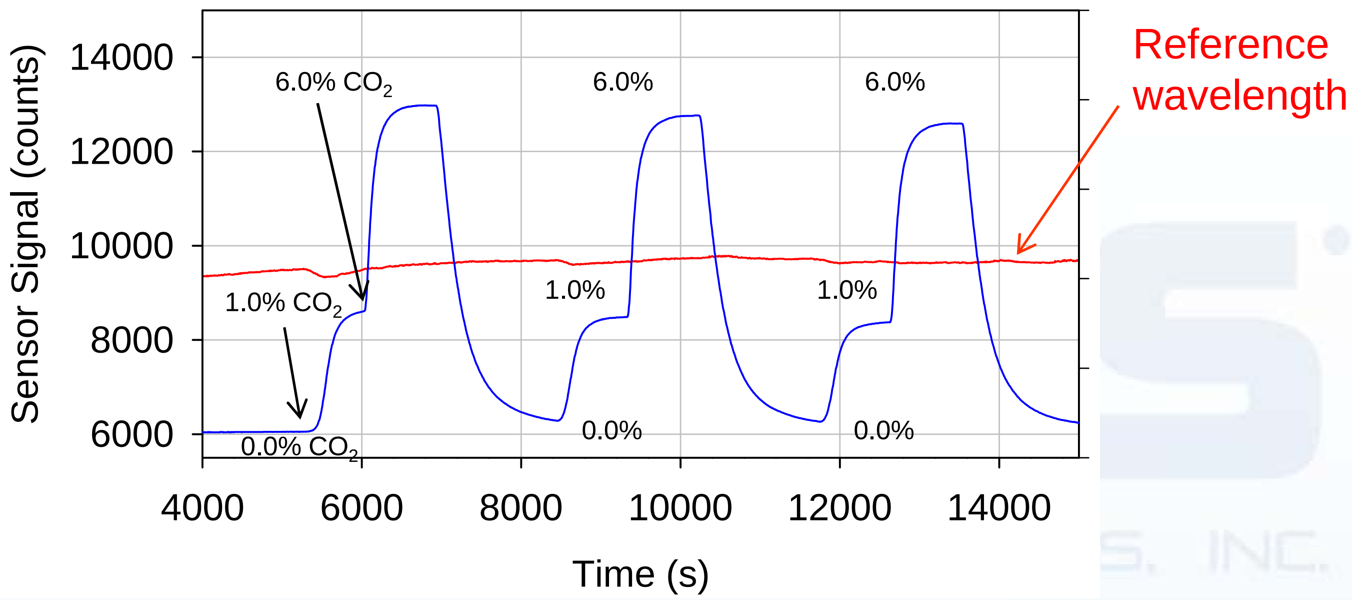
- A silica glass core fiber is coated with a polymer cladding containing a colorimetric indicator
- Upon exposure of any segment of the fiber, the CO_2 diffuses into the cladding and changes color
- A change in fiber attenuation at wavelengths relating to the color change is detected.





(Left) Fiber structure of colorimetric distributed fiber optic sensors; (right) fiber optic CO_2 sensor rolled onto a spool. Microscopic detail shows uncoated fiber, and fiber coated with the sensitive cladding.

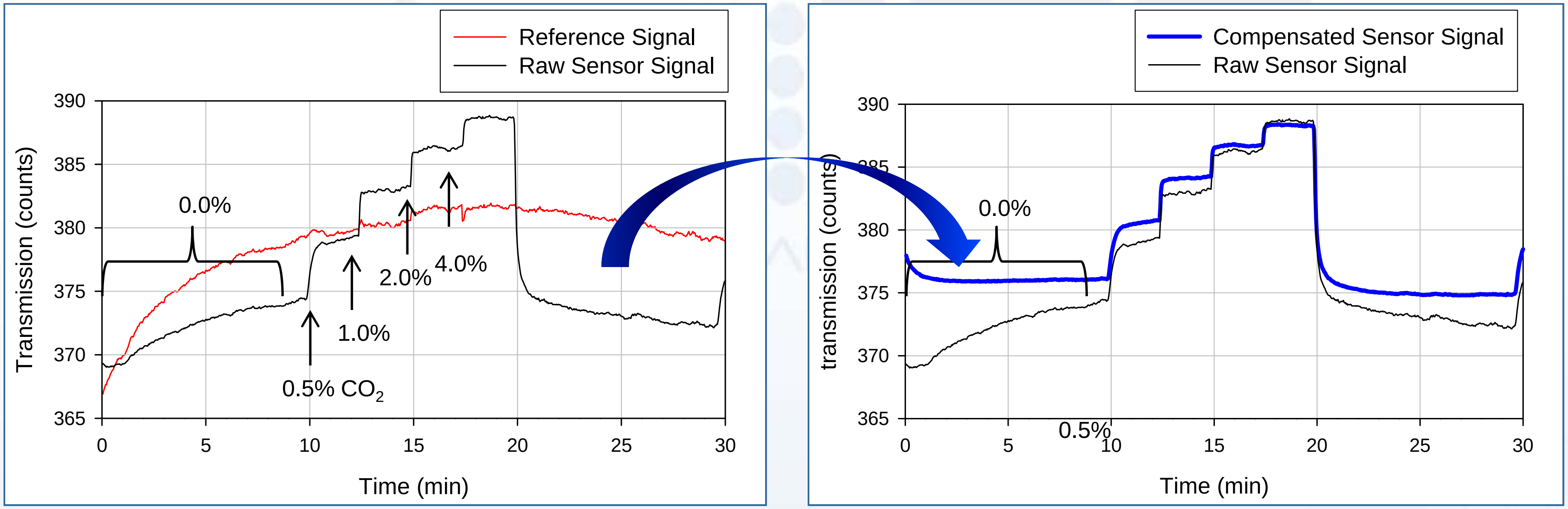
Technology



- The extent of color change (or attenuation change) depends on the concentration of CO_2, and is reversible
- Wavelengths far from the absorbance of the indicator dye are unaffected by the presence of CO_2, which enables the system to be self-referenced.

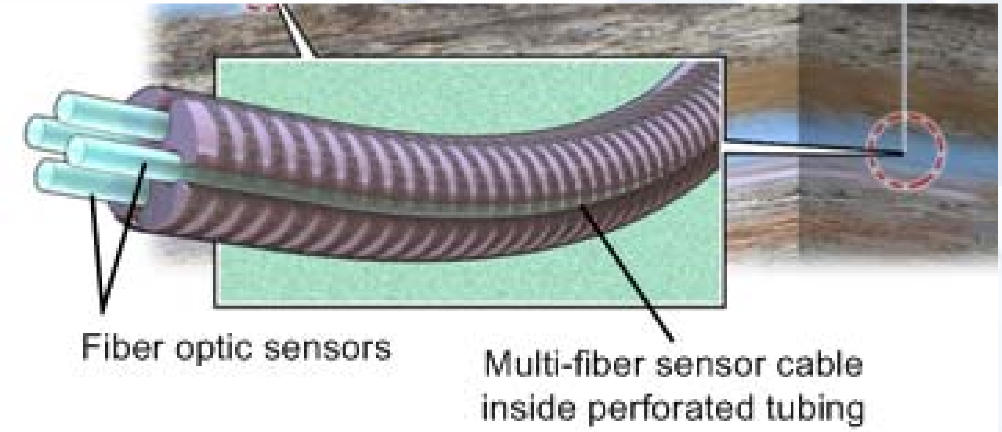
Technology

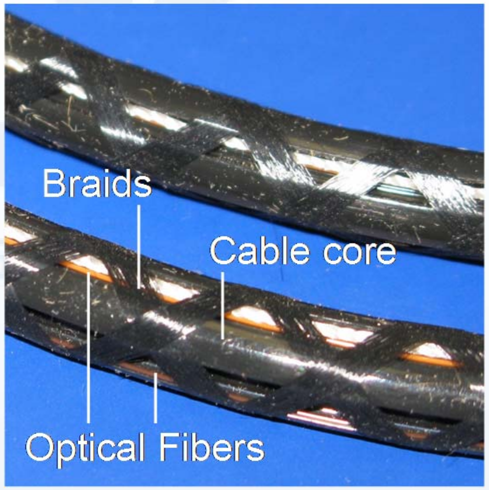
Wavelengths far from the absorbance of the indicator dye are minimally, or completely, unaffected by the presence of CO_2, **enabling the system to be self-referenced.**



Technology:
Sensor Protection for Field Deployment

In sensor system deployment, the sensor fibers must be **mechanically protected within a cable**, while simultaneously allowing the **free exchange of gases and water** between the environment and the sensor fibers.





Project History

SBIR Project (2010 – 2013)

Distributed Sensors for Dissolved CO_2

Core Technology

- Distributed fiber optic sensor for pH
- Distributed fiber optic sensor for salinity
- Multi sensor unit incorporating CO_2, pH, salinity, and temperature sensors
- Sensor network

- Advanced sensors for CO_2 (at high T and P)
- Readout unit for long sensors (>2 km)
- Deployment system and sensor cables for downhole monitoring

- Distributed fiber optic sensor for O_2
- Distributed fiber optic sensor for H_2O
- Multi sensor unit incorporating CO_2, O_2, humidity, and temperature sensors

Dissolved CO_2 in aquifers

Downhole CO_2 monitoring

Near-surface leaks into the atmosphere

Project Objectives

SBIR Project (2010 – 2013)

Distributed Sensors for Dissolved CO_2

Core Technology

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Dissolved CO_2 in aquifers

Downhole CO_2 monitoring

Near-surface leaks into the atmosphere

Project Phases

Phase I

- Development of advanced intrinsic fiber optic sensors and readout (length up to 2,500 ft. and able to withstand corrosive liquids).

Phase II

- Sensor evaluation and demonstration in simulated subsurface conditions.

Phase III

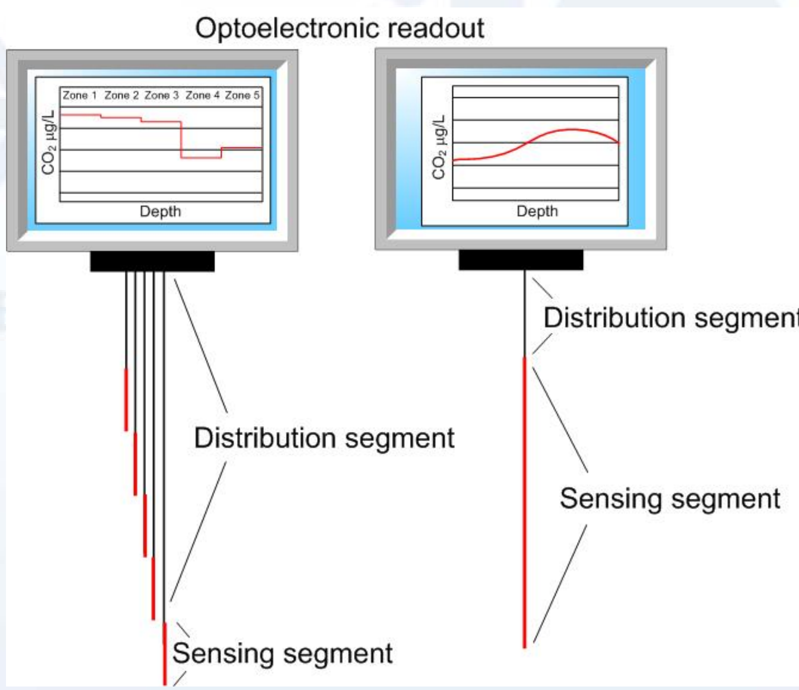
- Subsurface sensor deployment and operation (in a 5,900 ft. deep well at up to 2,000 psi).

Progress: *Optoelectronic Unit*

Develop an optoelectronic unit for remote operation.

Preliminary design – select **zone-by-zone** or **OTDR** approach based on *cable range* and *cable coverage.*

Zone-by-zone:
Better sensitivity
Longer range

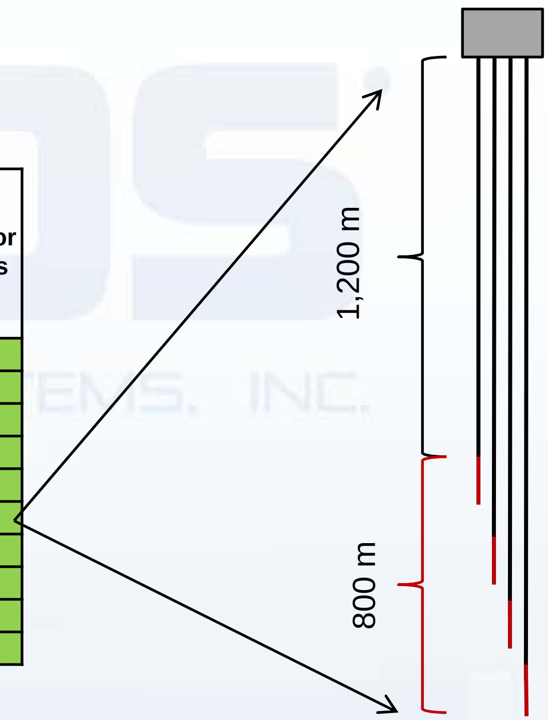


OTDR:
Better spatial resolution

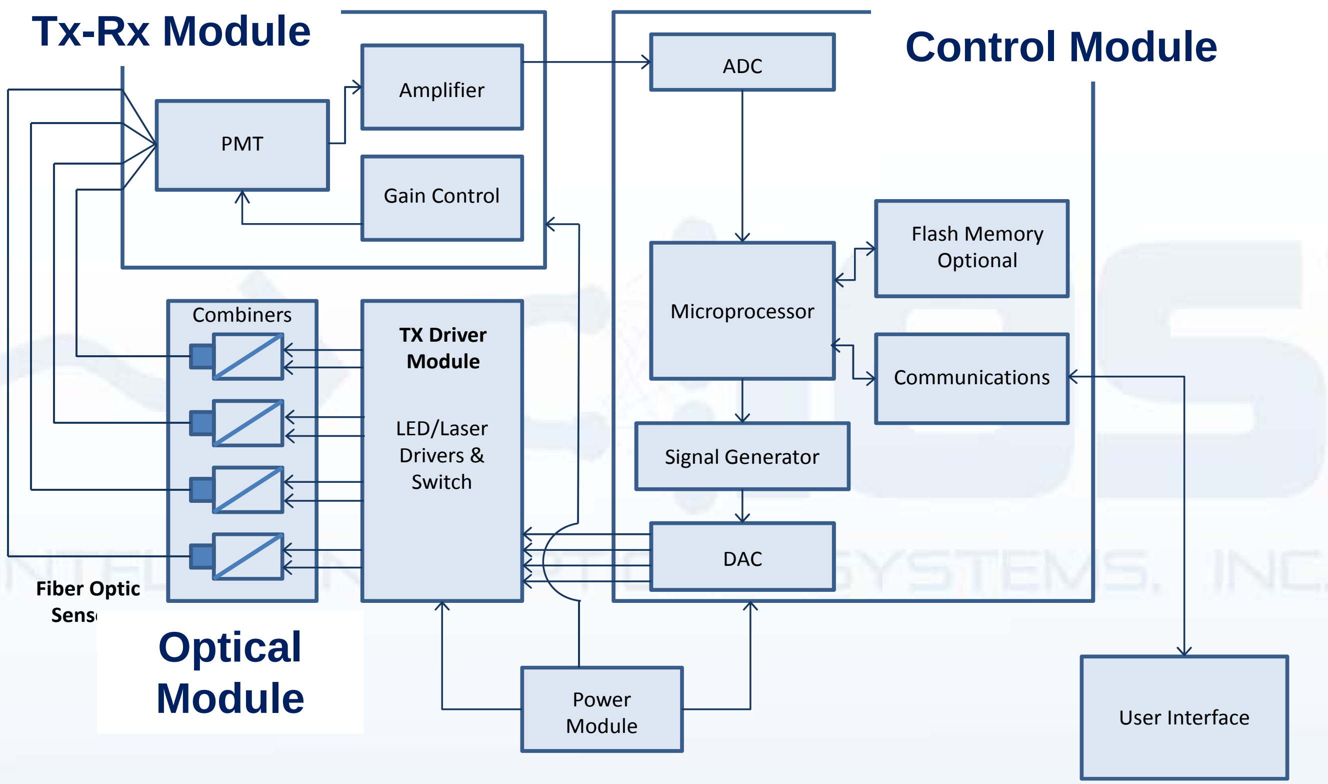
Progress: *Optoelectronic Unit*

The **zone-by-zone** approach was selected based on calculations that showed the feasibility of this design in meeting the *cable range* requirement (up to 2,500 ft.).

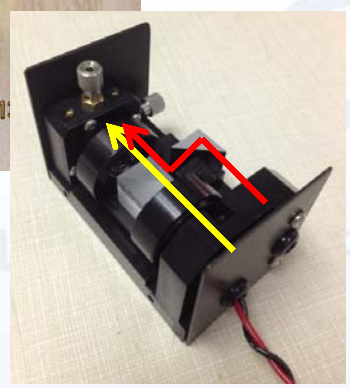
Distribution Fiber Length (m) (each segment)	Distribution Fiber Attenuation (dB)	Sensing Segment Length (m)	Sensing Segment Attenuation (dB)	Total Attenuation (dB)	Cable range (m)	Cable Coverage for 4 segments (m)
1,000	20	25	2	21	1,000	200
1,000	19	50	4	23	1,000	400
1,000	18	100	7	25	1,000	800
2,000	40	25	2	41	2,000	200
2,000	39	50	4	43	2,000	400
2,000	38	100	7	45	**2,000**	**800**
3,000	60	25	2	61	3,000	200
3,000	59	50	4	63	3,000	400
3,000	58	100	7	65	3,000	800
3,000	55	250	18	73	3,000	1,000

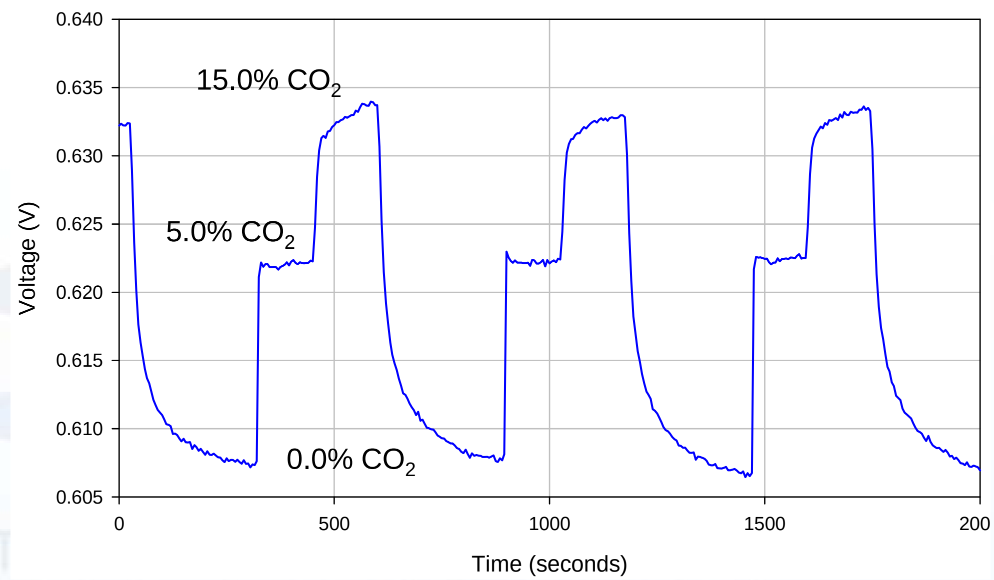


Progress: *Optoelectronic Unit*



Progress: *Optoelectronic Unit, Cable Range*





Fiber optic sensor cable with length of 2,100 m (6,890 ft.)

Average (5% CO_2) = 0.6223 V

Standard Deviation (n=25) = 0.0005 V

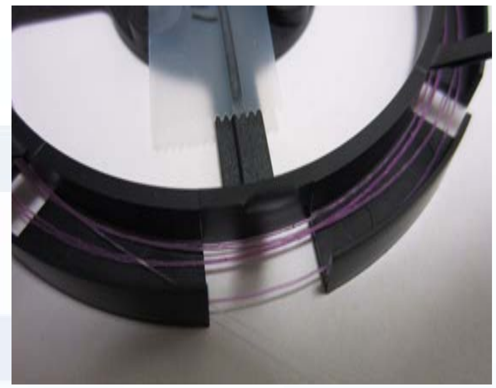
Noise to Signal = 0.08%

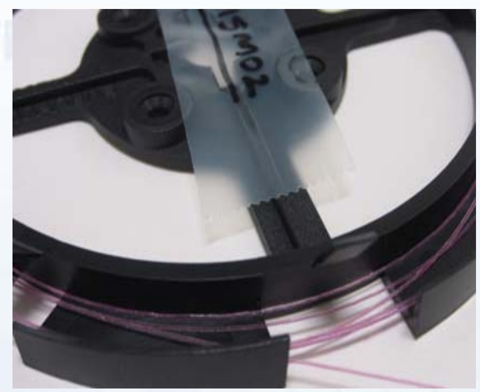
Progress: *Advanced Sensor Materials*

Films coated on glass slides

1. Fabrication of films
2. Evaluation of optical and chemical properties
3. Selection of candidate formulations
4. Fabrication of fiber sensor
5. Preliminary testing
6. Further characterization/ fabrication of films

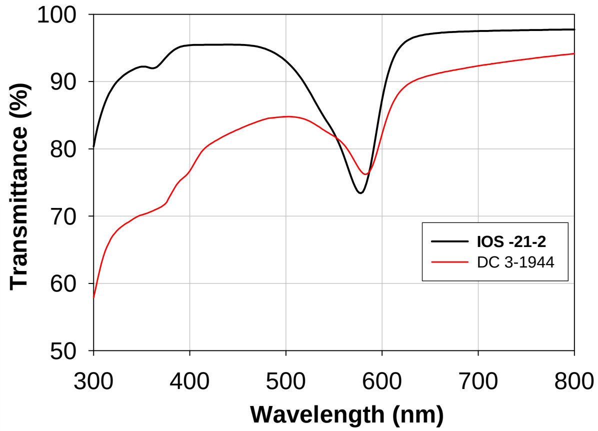
Fiber optic sensor prototypes



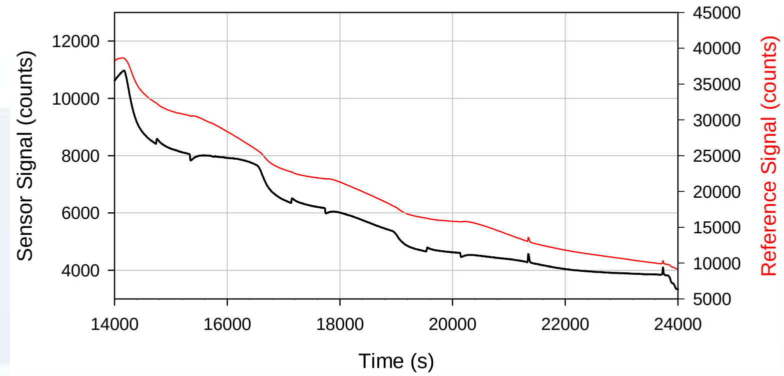


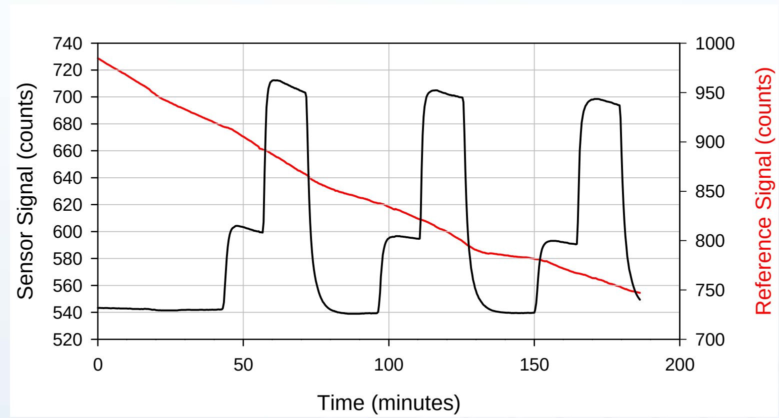
Progress: *Advanced Sensor Materials*

- Transmission



- Thermal stability



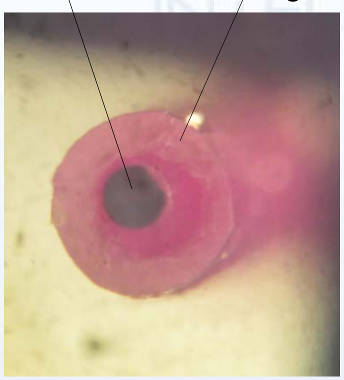


- Sensitivity and reversibility
- Attachment to glass
- Chemical stability
- Resistant to water immersion

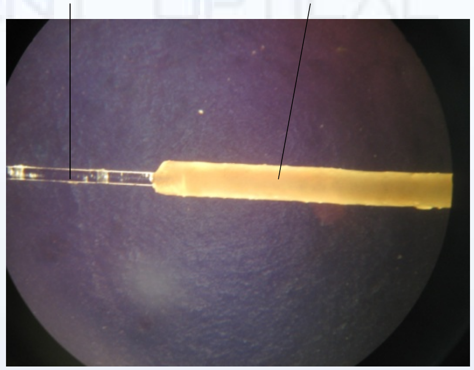
Progress: *Fiber Optic Sensor Production*

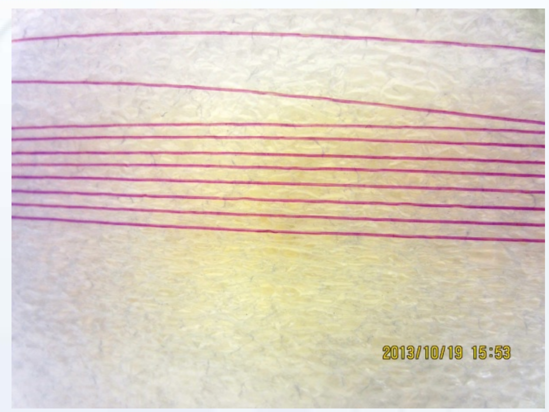
In the production of sensor prototypes, we use pre-fabricated silica glass "thread" as the core material, and apply the polymer cladding to the fiber with an optical fiber spooling machine, custom-built for fiber coating applications.

Glass core
Polymer cladding

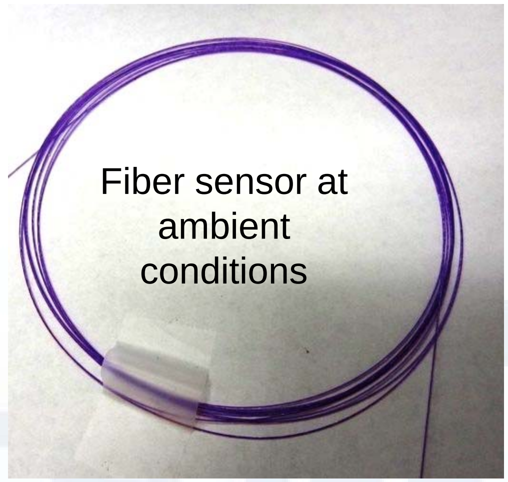


Uncoated fiber
Coated fiber

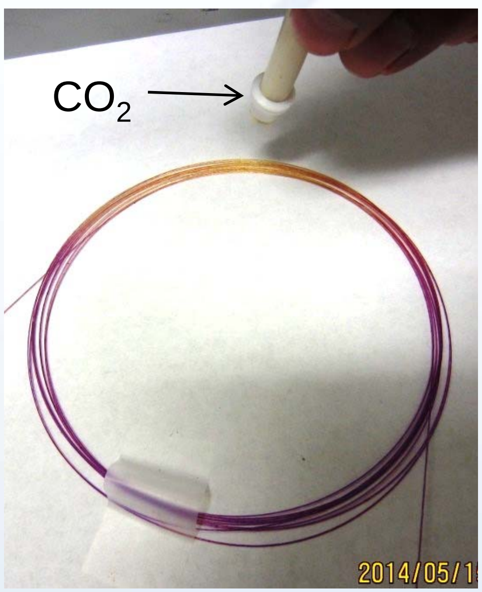




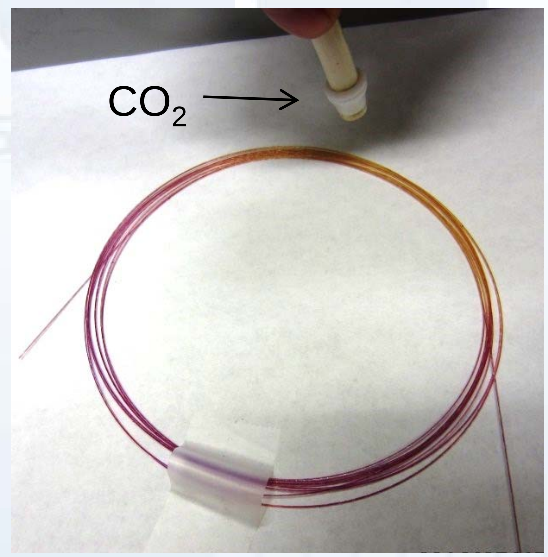
Progress: *Sensor Testing*



V1



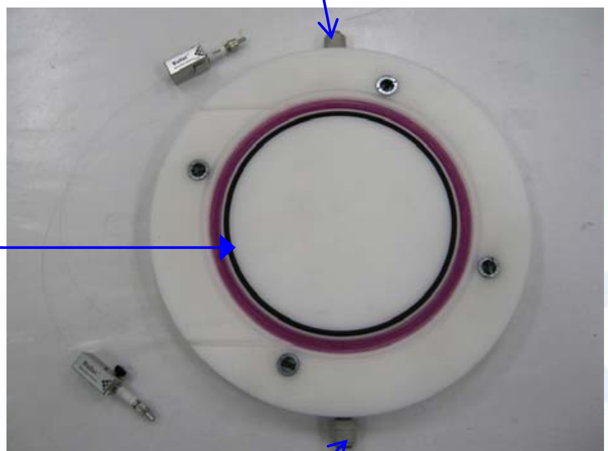
V2



Progress: *Sensor Testing*

Gas/water input

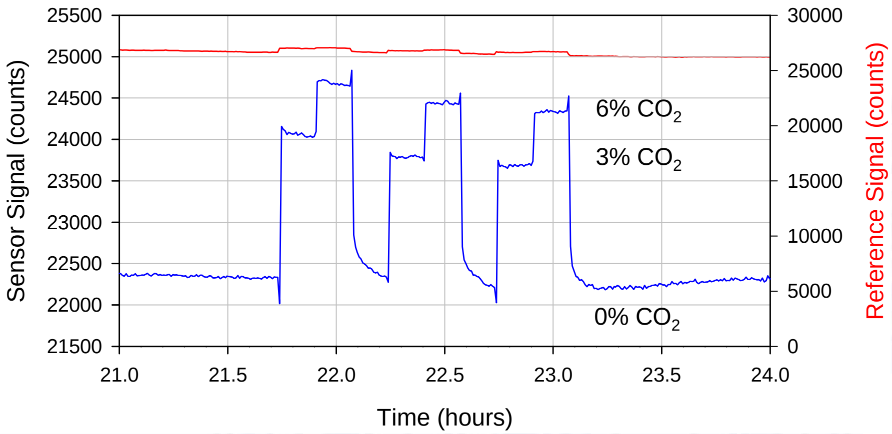
Fiber optic sensor segment



Gas/water output

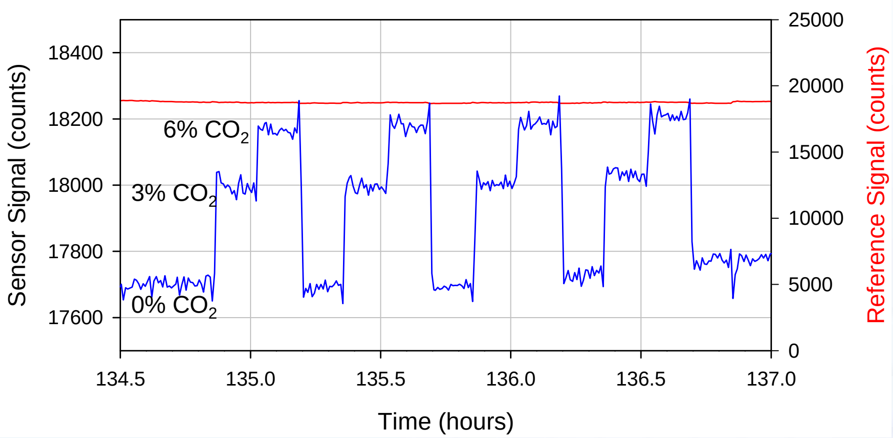
Progress: *Sensor Testing at Elevated Temperature, Gas Phase*

Temperature 80ºC



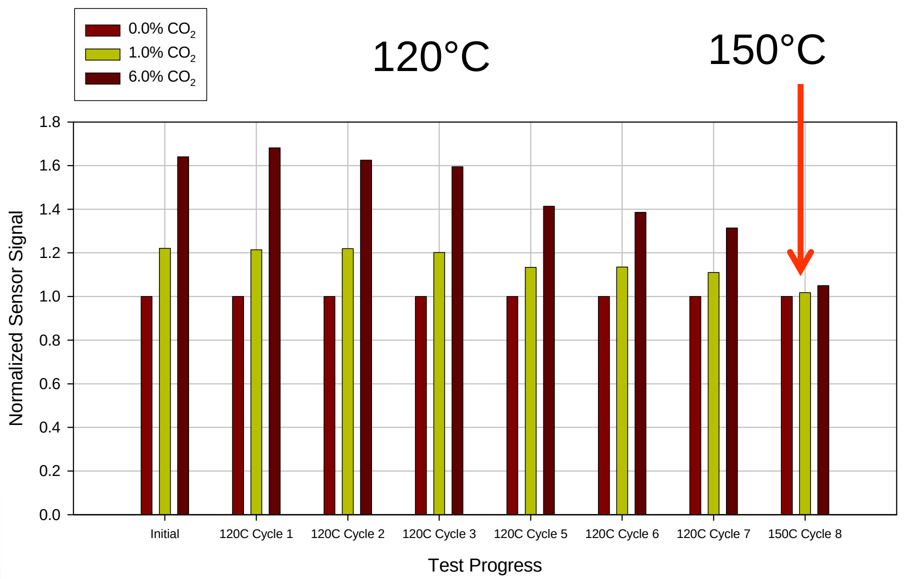
As expected, sensitivity is reduced with increased temperature.

Temperature 100ºC

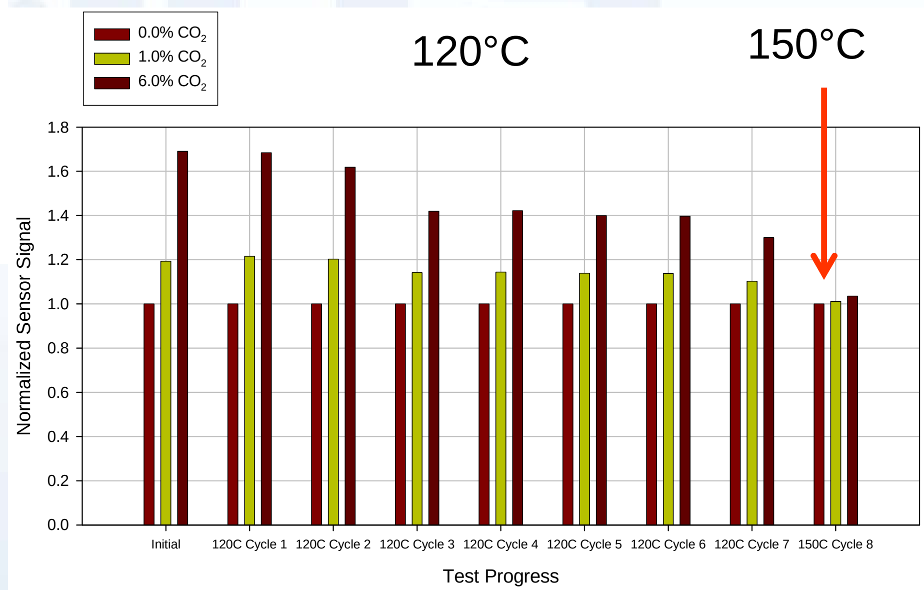


Progress: *Sensor Testing at Elevated Temperature, Gas Phase*

Accelerated Degradation Test



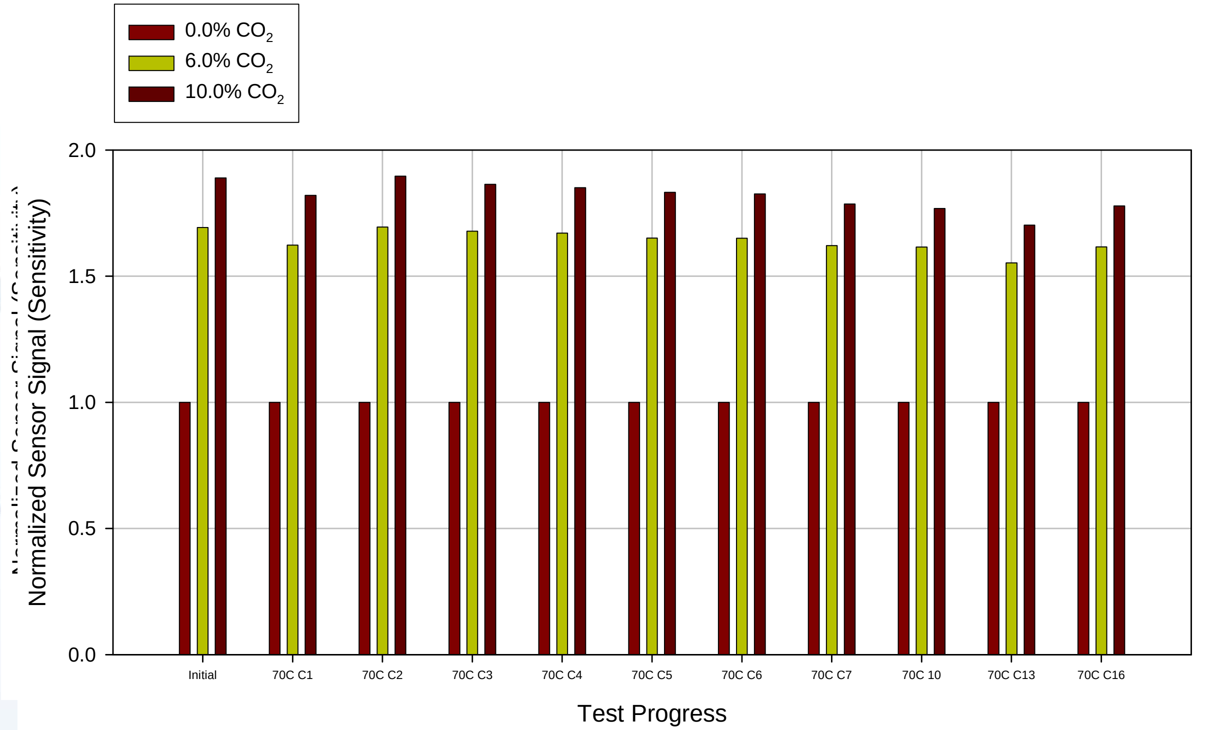
- The fiber sensors are exposed to cycles of elevated temperature and ambient temperature.



- Fiber sensors withstand 120°C
- Significant degradation at 150°C

Progress: *Sensor Testing at Elevated Temperature, Dissolved CO_2*

Accelerated Degradation Test



- Improved sensor formulations are stable at 70°C, the maximum temperature tested.
- Tests at higher temperatures must be conducted at pressure.

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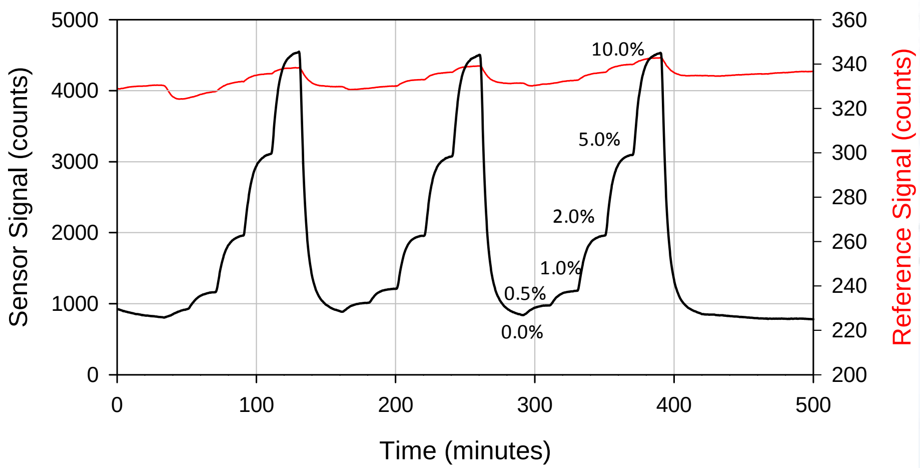
Progress: *Sensor Testing at Extreme Conditions, Dissolved CO_2*

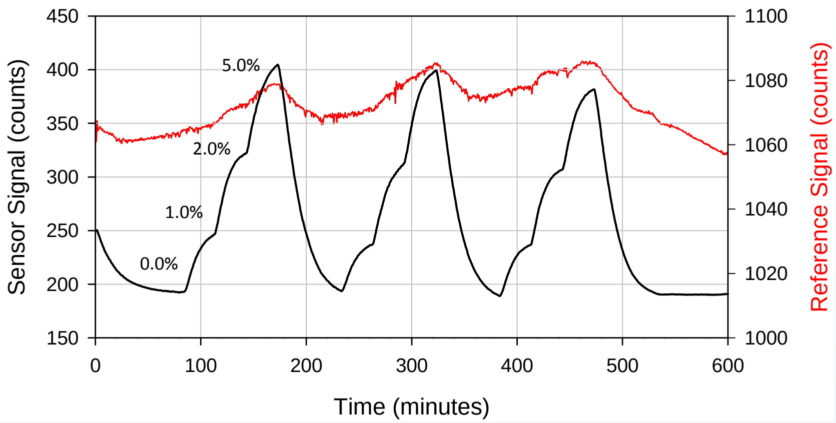
Standard conditions:

Sensitivity, reversibility, measurement range



Corrosive liquids:

Acid matrix (pH = 4.0)

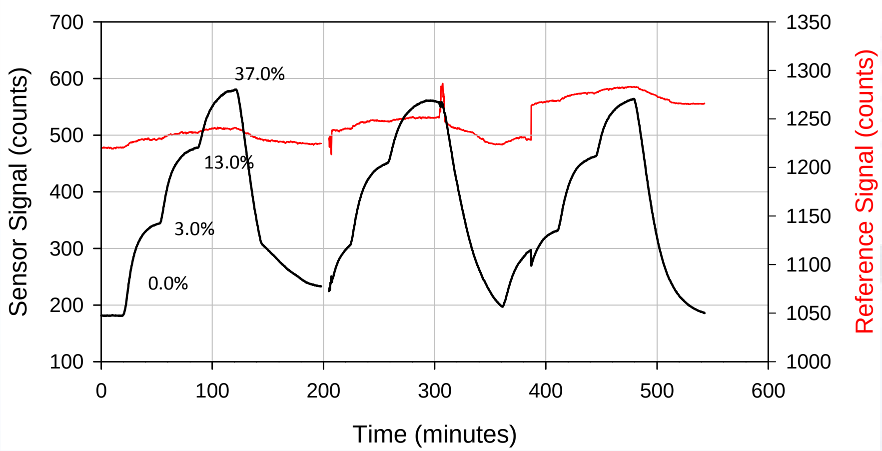


Response profiles of a CO_2 fiber optic prototypes immersed in a pH 4.0 solution equilibrated with four levels of CO_2

Progress: *Sensor Testing at Extreme Conditions, Dissolved CO_2*

Corrosive liquids:

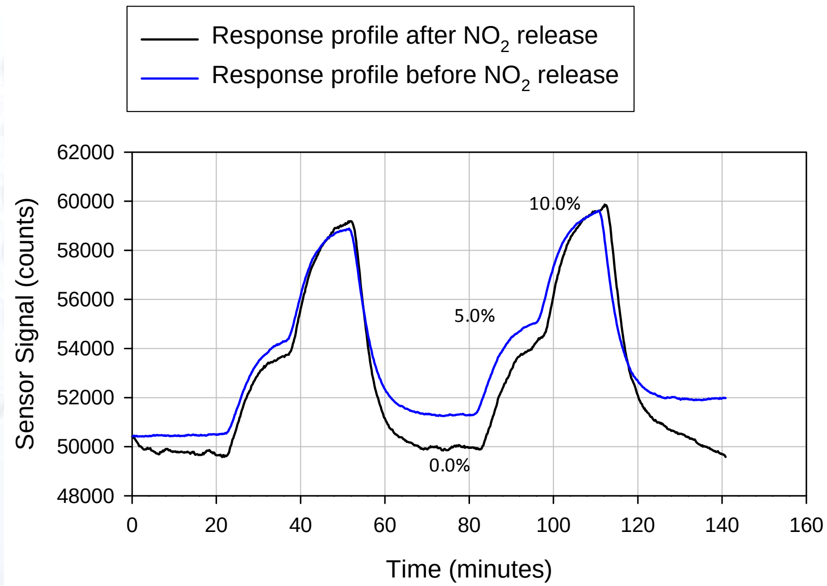
High salinity (250,000 ppm NaCl)



Response profiles of CO_2 fiber optic prototypes immersed in a 250,000 ppm NaCl solution equilibrated with four levels of CO_2.

Corrosive liquids:

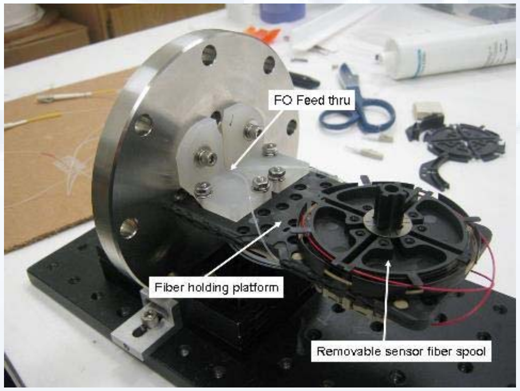
Traces of NOx or SOx (40 ppm NO_2)

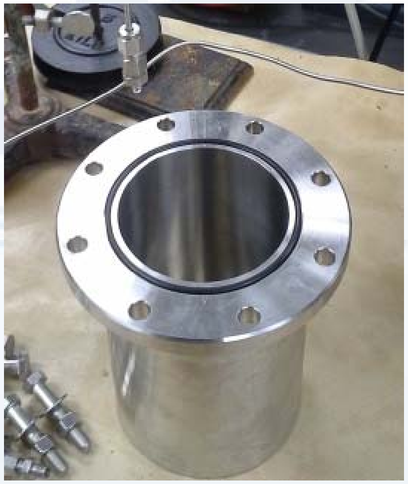


Response profiles of CO_2 fiber optic prototypes immersed in solution before and after equilibration with traces of NO_2 (40 ppm) and equilibrated with three levels of CO_2.

Ongoing and Planned Work

- **Perform Accelerated Degradation Testing**
  - High flow rates of corrosive water, exposure to highly biologically-contaminated media, exposure to temperature cycles, exposure to high power illumination…
- **Evaluate sensors at elevated pressure**

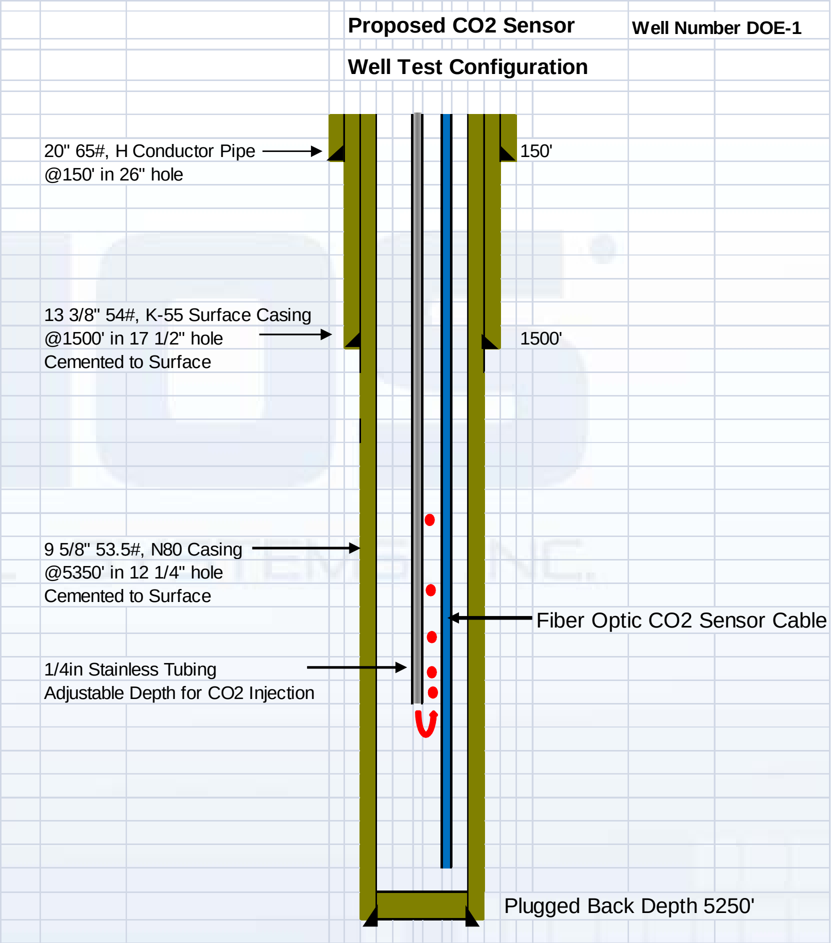




- **Perform analytical characterization of sensor system**

Ongoing and Planned Work

- Design and test sensor cables
- Design and assemble sensor deployment system
- Sensor deployment and validation in the field.



Conclusions

- A fiber optic sensor for **CO_2 monitoring in gas phase,** capable of operating at elevated temperatures, has been demonstrated.
- A fiber optic sensor for **dissolved CO_2 monitoring in aqueous matrixes,** capable of operating in corrosive environments and at elevated temperatures, has been demonstrated.
- **Instrumentation** demonstrating satisfactory performance while operating sensor cables 2 km long has been developed. Calculations predict continued good performance for sensors 3 km and even longer.
- Test at elevated pressure will be performed in the following months.

- The project is on schedule, and there is no technical impediment to conducting downhole monitoring

Conclusions

The Oil Industry is watching THE PROJECT...

Shell : *There is a high level of interest in you company CO_2-related projects*

Participants

Intelligent Optical Systems, Inc.: **Sensor development**

Jesús Delgado Alonso and Robert A. Lieberman

Bureau of Economic Geology at UTA: **Sensor field validation and modeling**

Changbing Yang

GeoMechanics Technologies: Downhole sensor deployment

Michael S. Bruno

Benson Laboratory at Stanford University: Sensor laboratory testing

Prof. Sally Benson and Ferdinand F. Hingerl

Montana State University (ZERT): Sensor field validation

Kevin Repasky

NETL Department of Energy

Barbara Carney, Robie Lewis, Robert Noll, Joshua Hull