# Real-time in-situ CO<sub>2</sub> Monitoring (RICO<sub>2</sub>M) Network for Sensitive Subsurface Areas in CCS

Project Number DE-FE0012706



### **Sensor Development**

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### **Sensor Field Validation and Modeling**

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U.S. Department of Energy
National Energy Technology Laboratory
2015 Carbon Storage R&D Project Review Meeting
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## **Outline**



- Benefit to the Program
- Technology
- Project Overview
- Technical Status
- Project Summary
  - Accomplishments
  - Planned work
- Acknowledgments



# **Benefit to the Program**

- Carbon Storage Program goal being addressed:
  - Develop and validate technologies to ensure 99% storage permanence.

#### Benefits Statement:

The project will develop a sensor network based on distributed fiber optic sensors for in-situ, real-time monitoring of geochemical parameters in groundwater. The system will be capable of covering large areas and measuring very low concentrations of CO<sub>2</sub> with high resolution, detecting small changes from background concentrations in sensitive areas. This technology contributes to the Carbon Storage Program's effort of ensuring 99% CO<sub>2</sub> storage permanence (Goal).



# **Benefit to the Program**

Monitoring groundwater in-situ and in real time to detect and measure very low concentrations of CO<sub>2</sub> with high resolution.

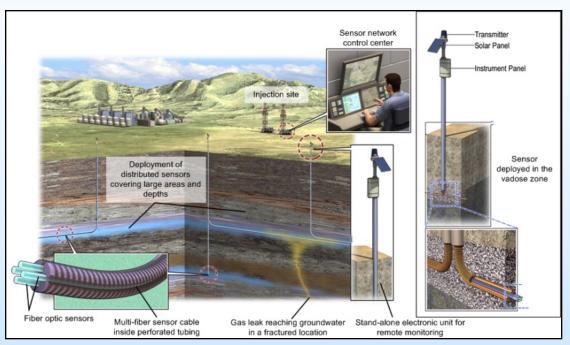
- Monitoring dissolved carbon dioxide is the most direct way to detect and quantify a leak reaching underground sources of drinking water.
- Current methods for detecting CO<sub>2</sub> leakage in groundwater are adapted from traditional groundwater quality studies – water samples are collected periodically and analyzed in the laboratory.
  - Not cost-effective for long-term monitoring of large areas
  - De-gassing during the sampling process can degrade accuracy
  - Very poor spatial coverage
  - Intermittent monitoring can miss changes in the geochemical parameters of groundwater.



### **Distributed Intrinsic Fiber Optic Chemical Sensors**

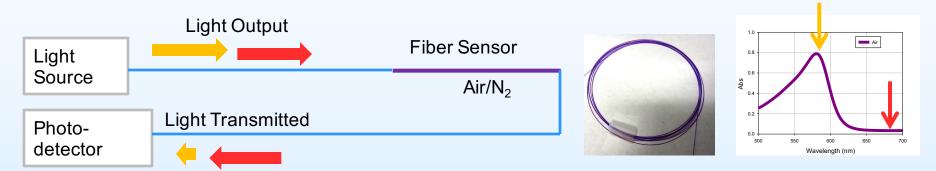
### **Unique Characteristics**

- The entire length of the fiber is a sensor
- Direct detection of dissolved CO<sub>2</sub>
- A single cable may include CO<sub>2</sub>, pH, salinity and temperature sensors.



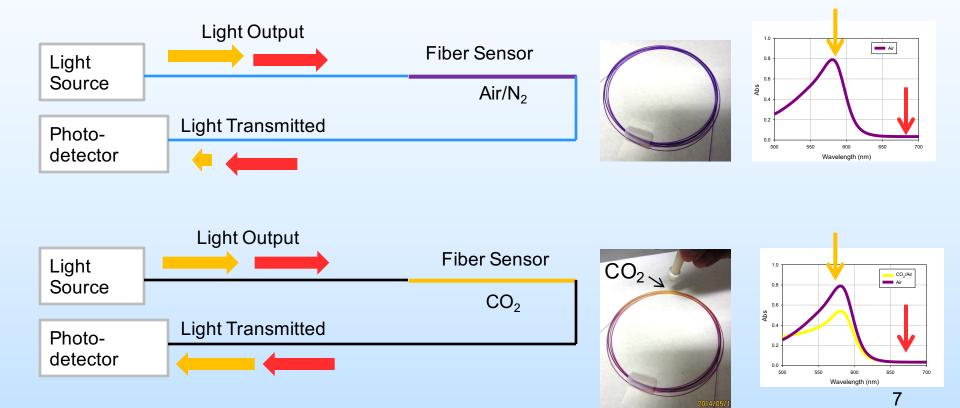


- A silica glass core fiber is coated with a polymer cladding containing a colorimetric indicator, which absorbs light at a particular wavelength.
- A light source is placed at one end of the fiber and a photodetector at the other end, and light transmission is measured.



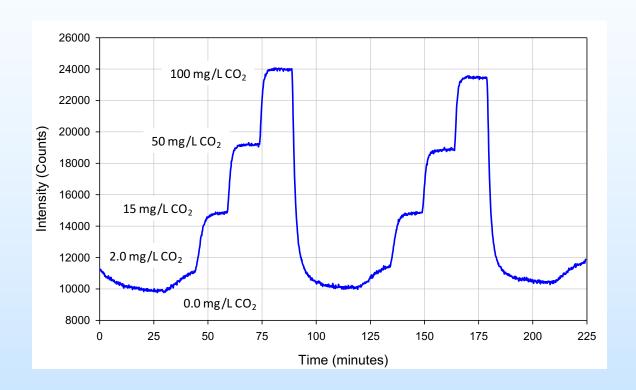


• Upon exposure of any segment of the fiber, the CO<sub>2</sub> diffuses into the cladding and changes color. The light transmitted through the fiber at wavelengths absorbed by the indicator varies with the concentration of CO<sub>2</sub>.

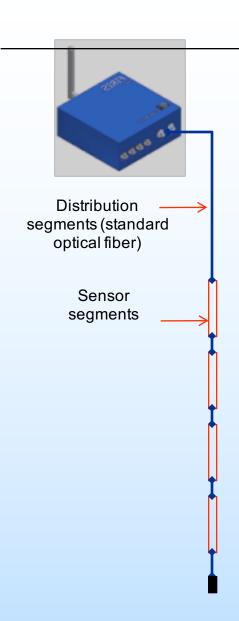




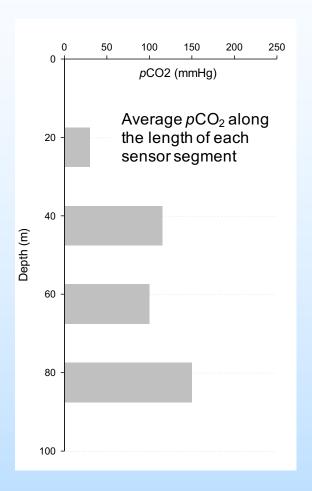
• The change in the fiber attenuation is **proportional** to the CO<sub>2</sub> concentration, and is **reversible**.

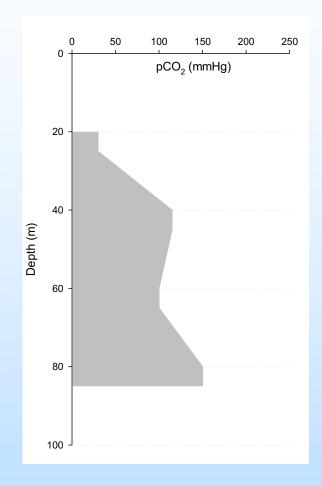






 Zone-by-zone monitoring using a sensor cable with multiple sensor segments.





# **Project Overview Goals and Objectives**



 Phase I Objective: Develop a multi-parameter system for highly sensitive and accurate detection of CO<sub>2</sub> in groundwater.

 Phase II Objective: Perform large-scale field deployment and demonstration of intelligent real-time, in-situ monitoring network (RICO<sub>2</sub>M Net).

# **Project Overview Goals and Objectives**



### Research Plan

- PHASE I: Develop a multi-parameter system
  - Generate system requirements
  - Select existing sensors (developed by IOS) for dissolved CO<sub>2</sub>
  - Develop fiber optic sensors for pH
  - Develop fiber optic sensor for salinity
  - Build and validate a monitoring system in the laboratory.

# **Project Overview Goals and Objectives**

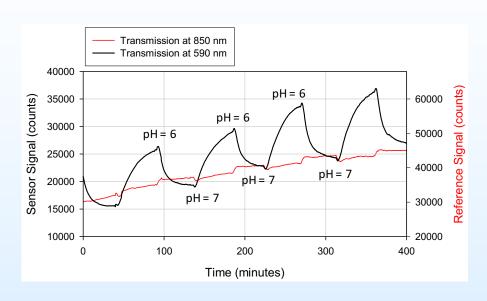


### Research Plan

- PHASE II: Perform deployment and demonstration in the field
  - Fabricate the monitoring sensor network
  - Deploy and continuously monitor geological parameters in groundwater (10-15 units for one year)
  - Validate results with established monitoring techniques
  - Perform controlled-release tests of CO<sub>2</sub> (measuring low concentrations of CO<sub>2</sub> with high accuracy).



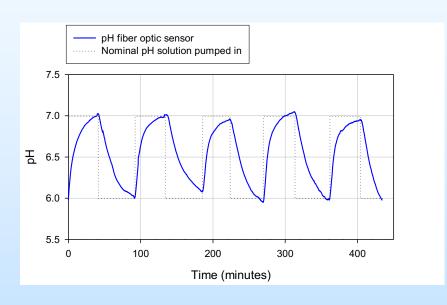
### Progress: Develop Distributed pH Sensors



#### **Basic Sensor Characteristics**

- Measurement range: 5 to 8.5 pH
- Resolution (precision): 0.04 (at 7 pH)
- Temperature range: 5°C to 30°C
- Temperature compensation: 1.4%/°C

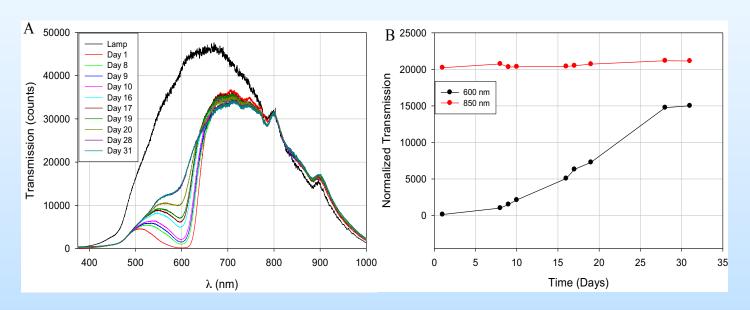






# Progress: Develop Distributed pH Sensors Indicator Retention in the Polymer

- Electrostatic retention by interaction with cationic groups in the polymer
- Under high water flow rate we observe indicator migration to the water





# Progress: Develop Distributed pH Sensors Indicator Retention in the Polymer

 Covalent immobilization by cross linking with vinyl groups in the polymer.

HO
$$\frac{Ph_3PBr_2}{CH_3CN, r.t.} [R-SO_2Br] \xrightarrow{NH_2} R-SO_2NHCHCH_2$$

$$\frac{Ph_3PBr_2}{Et_3N, 0C - r.t.} R-SO_2NHCHCH_2$$

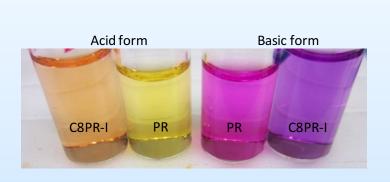
 Indicator dye with very low solubility in water by incorporating a long alquil chain.

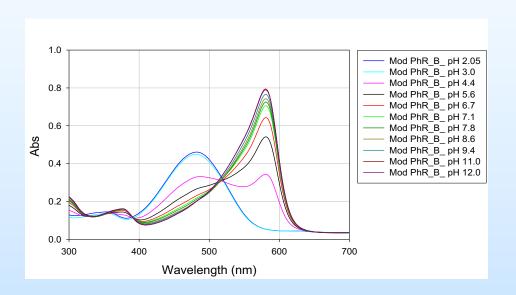
HO SO<sub>3</sub>Na 
$$\frac{Ph_3Br_2}{CH_3CN, r.t.}$$
 [R-SO<sub>2</sub>Br]  $\frac{CH_3(CH_2)_7-NH_2}{EteN, 0C-r.t.}$  R-SO<sub>2</sub>NH(CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>



# Progress: Develop Distributed pH Sensors Indicator Retention in the Polymer

 Indicator dye with very low solubility in water by incorporating a long alquil chain.

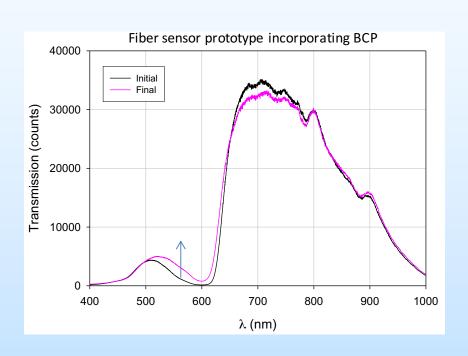


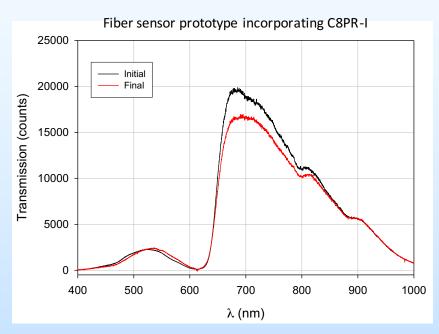




# Progress: Develop Distributed pH Sensors Indicator Retention in the Polymer

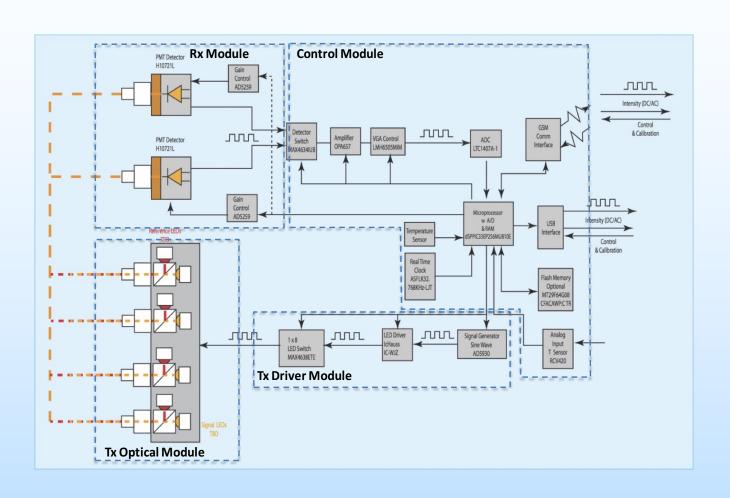
 Indicator dye with very low solubility in water by incorporating a long alquil chain.







### Progress: Design Multi-parameter Monitor





### Progress: Integrate Multi-parameter Monitoring System

#### **Control Module**





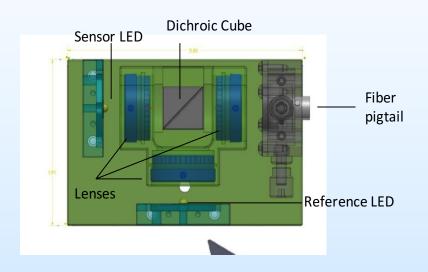
#### **Rx Module**

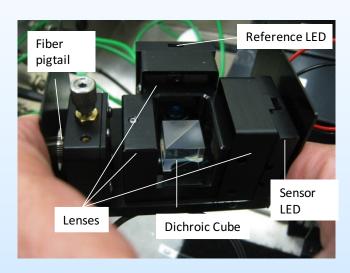




### Progress: Design Multi-parameter Monitor

### **Tx Optical Module**





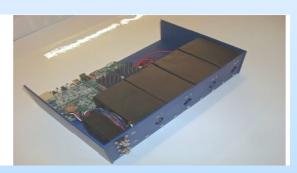


### Progress: Design Multi-parameter Monitor

#### RICO<sub>2</sub>M Multi-parameter Monitoring System









Simplified demonstrator assembled for first field evaluation

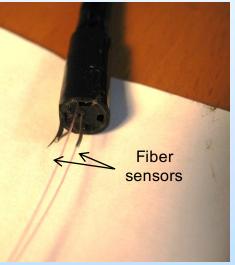


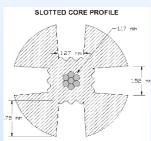
# Progress: Fabricate Multi-fiber Sensor Cables Sensor Cable Approach

**Advantages:** Possibility of fabricating long sensor segments, and narrow diameter of the cable.

**Challenge:** Assembling the fiber optic sensors, in particular the novel pH and salinity sensors.











# Progress: Fabricate Multi-fiber Sensor Cables Sensor Probe Approach

**Advantages:** Makes fabrication easier, and simplifies storage and shipping.

**Limitation:** Applicable only where significant spatial coverage is not required.







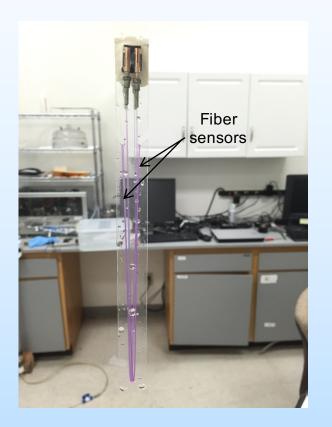
# Progress: Fabricate Multi-fiber Sensor Cables Sensor Probe Approach

**Advantages:** Makes fabrication easier, and simplifies storage and shipping.

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Sensor probe

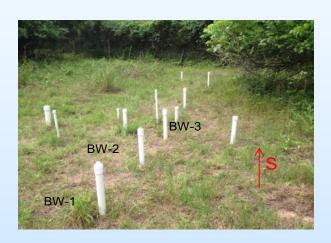




### Progress: Deploy Sensor System at Aquifers

# The Brackenridge Field Laboratory (BFL)

is an 82-acre research site with a siliclasticdominated alluvial aquifer adjacent to the Colorado River in Austin, Texas.



#### The Devine Test Site (DTS)

is a 100-acre site less than 50 miles southwest of San Antonio in Medina County, Texas.



A Class V well authorization for the project at the Brackenridge Field Laboratory has been secured.



### Progress: Deploy Sensor System at Aquifers

First system assembly for field test



**Demonstrator units** 

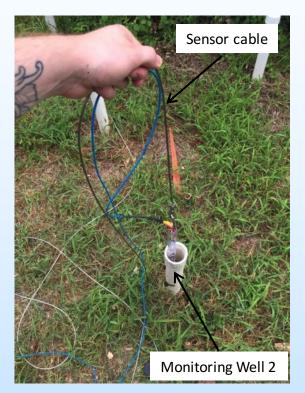
#### Distribution cable





### Progress: Deploy Sensor System at Aquifers



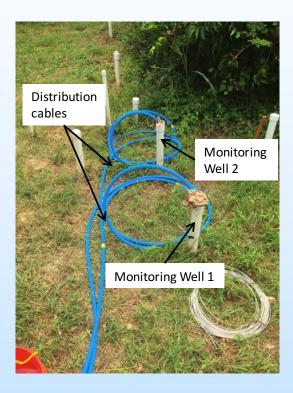




### Progress: Deploy Sensor System at Aquifers





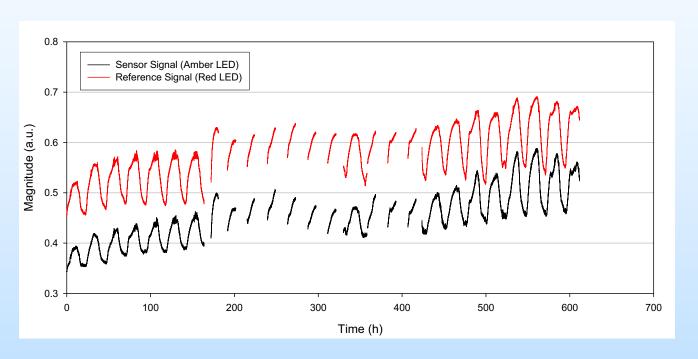




### Progress: Conduct Baseline Monitoring

### Field operation is always exciting!

**Challenges:** Interference from daylight in the measurements – error in the fabrication of the distribution segment. Calibration conducted in the laboratory has not yet been applied in the field.

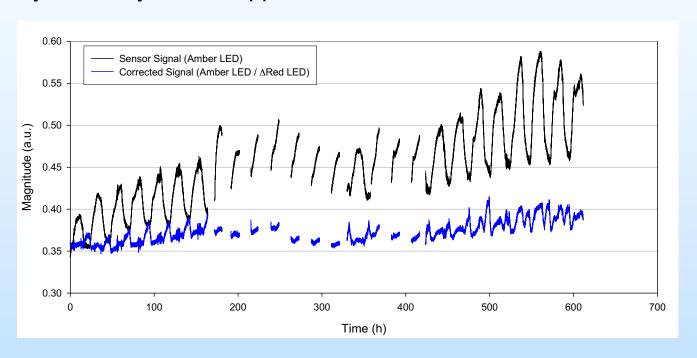




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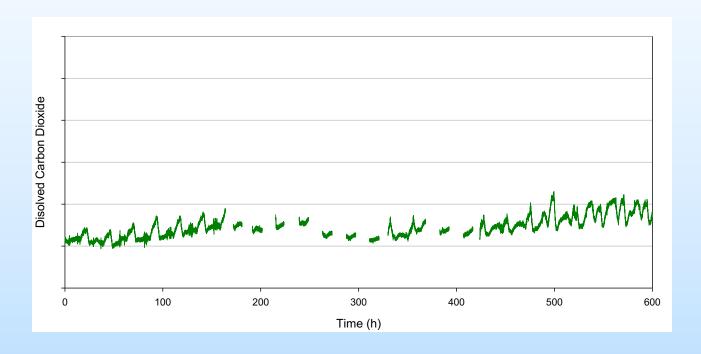




### Progress: Conduct Baseline Monitoring

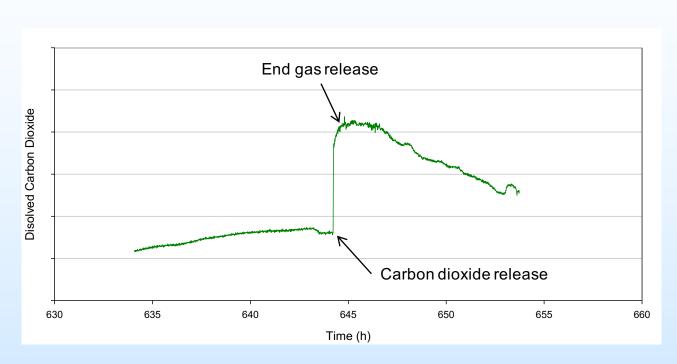
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### **Progress: Controlled Carbon Dioxide Release**





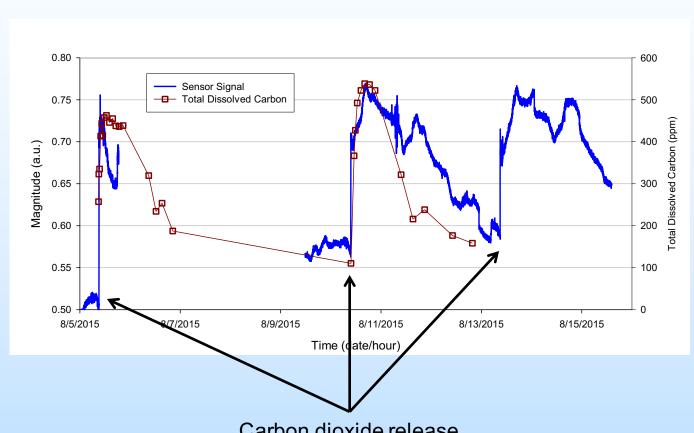


Water sampling pump

Carbon dioxide release tube



### Progress: Controlled Carbon Dioxide Release







Carbon dioxide release

# INTELL

# Summary Accomplishments to Date

- Designed, fabricated, and integrated the first version of the optoelectronic unit for the fiber optic multi-parameter monitor.
- Assembled a simplified version of the optoelectronic unit to perform the first field studies.
- Designed and fabricated sensor cables and, as an alternative design, sensor probes.
- Assembled and deployed in the field the first multi-parameter monitor using the simplified demonstrators. Identified and implemented necessary system adaptation for field operation.
- Conducted a first CO<sub>2</sub> controlled-release test.

# **Summary Planned Work**



- Verify opto-electronic unit incorporating complete functionality (RICO<sub>2</sub>M v1.0).
- Deploy first generation RICO<sub>2</sub>M v1.0 system.
- Monitor performance of v1.0 systems in the field for several months.
- Assemble and deploy in the field the second generation RICO<sub>2</sub>M system (v2.0).
- Compare results with established analytical techniques (determine accuracy).
- Demonstrate detection of CO<sub>2</sub> leaks by controlled-release tests (determine sensitivity).
- Advance and validate reactive transport modeling for CO<sub>2</sub> by comparison with continuous monitoring.



# **Acknowledgments**

### **NETL Department of Energy**

### Joshua Hull

Robie Lewis, Robert Noll, Barbara Carney

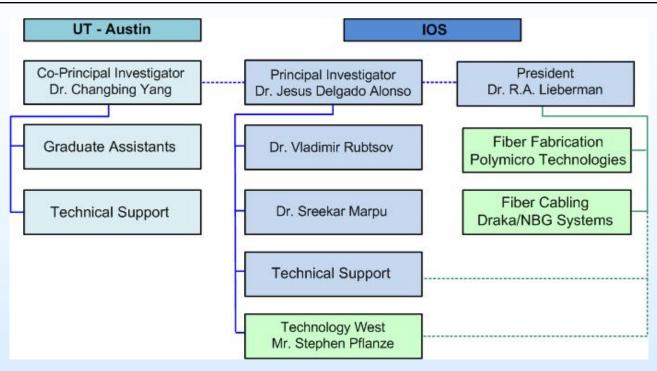


# Appendix

- Organization Chart
- Project Schedule
- Bibliography



# Organization Chart



As the prime contractor for this project, IOS will carry out all activities related to the design, fabrication, and testing of the distributed CO<sub>2</sub> sensor network, and will provide field support to the University of Texas at Austin (UT-Austin) throughout the system Phase II field trials.

UT-Austin will manage all aspects of CO<sub>2</sub> sensor system field testing, and will provide valuable technical guidance in Phase I, assuring that the system design meets the rigorous demands of the subsurface environment found at the CCUS test site.



# Organization Chart: Intelligent Optical Systems, Inc.

- Founded in 1998
- Business focus:
  - Chemical sensors
  - Biochemical sensors
  - Advanced light sources & detectors
- 25 employees; 9 PhDs
- 11,500 sq. ft. -- labs, clean rooms, offices
- \$8M in laboratory equipment

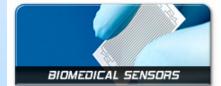














# Organization Chart: The University of Texas at Austin

### **Bureau of Economic Geology (BEG)**

- Established in 1909, BEG is the oldest research unit at The University of Texas at Austin
- Provide research and advice related to energy and environmental issues, and perform State Geological Survey functions as requested by the State Legislature.



### **Gulf Coast Carbon Center (GCCC)**

- Seeks to impact global levels of atmospheric carbon dioxide by:
  - Conducting studies on geological sequestration of CO<sub>2</sub> in the deep subsurface
  - Educating the public about risks that might limit deployment of geological sequestration and measuring the retention of CO<sub>2</sub> in the subsurface
  - Enabling the private sector to develop an economically viable industry to sequester CO<sub>2</sub> in the Gulf Coast area.





# Project Schedule

Tasks	Year 1										Year 2										Year 3											
	1	2	3	4	5	6	7	8 9	9 10	0 11	1 12	13	14	15	16	17 1	8 1	9 2	0 21	22	23	24	25	26 2	27 2	8 29	30	31	32	33 3	4 35	5 36
1. Management																						1 ::				- :	-					
2. System requirements																																
3. Sensor for pH																																
4. Sensor for salinity	100															.:																
5. Multi-fiber sensor cables	11		- 1																					1111		1.11	1					-
6. Multi-parameter monitoring unit	- "-																				- "			- 1								
7. Characterization in laboratory																																
8. Fabrication of network																													-			
9. Deployment and monitoring										1																						
10. Controlled-release field tests			-:			• :								1.			. :															
11. Design review																																
MILESTONES				1			:		2		3			4		5 6	5 7	7	8		- :			:	9		:			1	0	1

#### PHASE I: Develop a multi-parameter system

- Milestone 1. System Functional Requirement Document (FRD) generated.
- Milestone 2. Fiber optic distributed sensor for pH fabricated and characterized in the laboratory.
- Milestone 3. Fiber optic distributed sensor for salinity fabricated and characterized in the laboratory.
- Milestone 4. Monitoring system assembled and system operation verified in accord with FRD.
- Milestone 5. Multi-parameter monitoring system characteristics established.

#### PHASE II: Perform large scale field validation

- Milestone 6. Groundwater chemistry survey, using the traditional method, conducted.
- Milestone 7. First series of multi-parameter monitoring system fabricated.
- Milestone 8. First Intelligent Real-time in-situ CO<sub>2</sub> Monitoring Network ("RICO<sub>2</sub>M Net") deployed.
- Milestone 9. Revised multi-parameter monitoring systems fabricated and deployed.
- Milestone 10. RICO<sub>2</sub>M Net detects presence (or absence) of CO<sub>2</sub> in sensitive subsurface locations.
- Milestone 11. System design reviewed.