TAGGING CO$_2$ TO ENABLE QUANTITATIVE INVENTORIES OF GEOLOGICAL CARBON STORAGE
DOE AWARD #DE-FE0001535

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Presentation Outline

- Benefit to the program
- Project overview: Why $^{14}\text{C}$ for MVA?
- Technical status: Cartridges, injections, lasers
- Summary
- Organizational chart
- Collaborators
Benefit to the Program

• Develop technologies to demonstrate that 99 percent of injected CO₂ remains in the injection zones.

Permanent storage of CO₂ can be demonstrated by adding carbon-14 (¹⁴C) prior to injection. This research project aims to demonstrate this by tagging fossil CO₂ with ¹⁴C at a field site. When completed, this system will show that ¹⁴C can be a safe and effective tracer for sequestered CO₂. A laser-based ¹⁴C measurement method is being adapted for continuous monitoring. This technology contributes to the Carbon Storage Program’s effort of ensuring 99 percent CO₂ storage permanence in the injection zone(s) (Goal).
• **Project Overview: Why use $^{14}$C in MVA?**

• Radiocarbon, or $^{14}$C:
  – Long half-life radio isotope: $\tau_{1/2}=5730$ years
    • Produced naturally by cosmic radiation
    • Made artificially by neutron capture
  – Ambient concentration: $^{14}$C/$^{12}$C $\approx 10^{-12}$
  – Concentration in fossil fuels: $^{14}$C/$^{12}$C $< 10^{-14}$

• Fossil-based CO$_2$ has ~100x less $^{14}$C than natural (biogenic) CO$_2$

• $^{14}$CO$_2$ is chemically identical to $^{12}$CO$_2$ and can indicate fixation

\[ ^{14}\text{N} + n \rightarrow ^{14}\text{C} + p \]
Coal Use

100 pMC

Use

$^{14}$C tagging

Monitoring

Leakage?

<1 pMC

CO$_2$ storage

CO$_2$ → Ca(CO$_3$)?
Coal

>1 pMC

Plants → Process

100 pMC

Monitoring

Leakage?

CO$_2$ storage

CO$_2$ → Ca(CO$_3$)$_2$?
14C tagging

- Tag intended at ≈ 1 part per trillion
  - This limits subsurface concentration to ambient levels
  - Makes fossil based CO2 look like bio-based CO2
  - Requires 1 g 14CO2 per million ton CO2
- 1-day tag limits liability in the event of accidental release
• **14C filling station**
  
  – Produced calibrated SF$_6$-CO$_2$-water tag cartridges
  
  – Produced $^{14}$CO$_2$-water solutions with 190 pCi, 9.3 nCi and 37 nCi $^{14}$CO$_2$
• Tagging very large stream with very small tag (1 in $10^{12}$)
  • 1 g $^{14}$CO$_2$ for 1 M ton CO2
• Needs to demonstrate accuracy and precision
• Potential injection into super critical or liquid CO$_2$
• Needs to be demonstrated at lab scale and in field test
• Bench-scale high-pressure flow loop
  – Turbulent flow regime
  – Pressurized CO\textsubscript{2} flow loop to 1457 psi CO\textsubscript{2}, 33 °C, supercritical regime
  – Injected SF\textsubscript{6} solution into super critical CO\textsubscript{2} at the 100 part-per-trillion level with error of <5%
• We need a method to monitor, record, and control injection on-line and in real time
• Verification and accounting necessary at injection
• Standard methods are not viable for this application:
  • Accelerator Mass Spectrometry is a batch method
  • Liquid Scintillation Counting is too slow
• Development of laser-based currently pursued
• Development of $^{14}$CO$_2$ Detector
• IntraCavity OptoGalvanic Spectroscopy (ICOGS)
  – Initial results were very promising
  • Potential for fast, inexpensive, online $^{14}$C measurement at the part-per-trillion (Modern) level

Murnick et al., Analyt. Chem. 2008

Original positive results

Laser pulses repeatedly excite $^{14}$CO$_2$ molecules in a glow discharge
Which changes the discharge temperature
Which changes the discharge conductivity

Lenfest Center for Sustainable Energy
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• Development of $^{14}$CO$_2$ Detector

We can measure:
- Laser power
- Laser wavelength
- Cell pressure
- Sample flow rate
- OG voltage

We can control:
- Laser cavity position
- Laser modulation mode
- Cell pressure
- Sample flow rate
- Cell discharge power
• Laser-based $^{14}$CO$_2$ detector
  – Assembled Intra-Cavity Opto-Galvanic Spectrometer (ICOGS)

- Spectrum Analyzer
- IR camera
- Webcam
- $^{14}$CO$_2$ laser
- Oscilloscope
- Pressure controller
- Mass flow controllers
- Sample stage
- RF excitation and detection
- Valve to vacuum pump

• Not shown:
  • Turbo pump
  • NI CompactDAQ
  • NI programmable power supplies
• Detection circuitry
  – Designed new filtering and amplifying circuitry for OG signal
  – Revealed a large transient at short times
  – Attributed to the response of the buffer gas to large changes in laser power (~40 W)
  – Appears to dominate signal when the laser is operated by generating a series of laser pulses ("Chopping mode") at ~100Hz
• Cavity Modulation
  – Developed new signal generation method: Cavity modulation
  – Generates a signal by changing the length of the laser at ~100 Hz
  – Produces a smoothly varying change in power and laser wavelength
  – Signal generation with cavity modulation was confirmed by external OG cell measurement on $^{12}$CO$_2$.
  – Similar signal to noise ratio when measuring CO$_2$ concentration.

The deviation for cavity modulation (red) is shown against that of laser chopping (green) for $^{12}$CO$_2$. 

\[ y = 0.2024x^{-0.474} \quad R^2 = 0.8815 \]

\[ y = 0.0265x^{-0.299} \quad R^2 = 0.9122 \]
• Development of $^{14}$CO$_2$ Detector
  – We were unable to see a signal in Cavity modulation
  – Indicates that most, possibly all, of the measured signals have been background fluctuations
  – Comparison with HITRAN data highlights an adjacent $^{12}$CO$_2$ absorbance line, 200 – 111, P(19)e
  – Work to explain role of P(19)e in ICOGS data is underway...

Scans do not reveal an intracavity response with cavity modulation
• Prospects for $^{14}$CO$_2$ Detector
  – Recent publications out of Uppsala University in Sweden have also highlighted this lack of reproducibility
  – Earlier results from Columbia are now attributed to small confounding pressure changes between samples
  – We are currently looking to use highly enriched samples to establish a quantitative lower limit of detection
  – Detection may be easier on other $^{14}$CO$_2$ laser lines away from $^{12}$CO$_2$ lines

Murnick et al., Analyt. Chem. 2008

Persson et al., Analyt. Chem. 2013

Original, promising results

Recent results highlighting irreproducibility of original results
- Development of $^{14}$CO$_2$ Detector
  - $^{12}$CO$_2$ background lower at other $^{14}$CO$_2$ laser lines.

$^{14}$CO$_2$ line = 849.781825 cm$^{-1}$

$^{14}$CO$_2$ line = 851.489499 cm$^{-1}$

P(18)

P(20)
• Future Plans
  – Carry out $^{14}$C detector experiments with highly enriched samples (>1k Modern)
  – Inject $^{14}$CO$_2$ into laboratory high-pressure flow loop
  – Inject $^{14}$CO$_2$ at CarbFix pilot injection site in Iceland
Organizational Chart

**Columbia University**

- Klaus Lackner, PI: Oversight and development of 14C-detector
- Alissa Ah-Hyung Park, co-PI: Construction of high-pressure flow loop
- Juerg Matter, co-PI: Field tests at CarbFix site in Iceland

**Barnard College**

- Martin Stute, co-PI: Construction of 14C detector and filling station design
- Cantwell Carson, postdoc: Construction of 14C detector
- Yinghuang Ji, student: Construction of filling station, testing flow loop
Collaborators:

- University of Groningen
  - Harro Meijer
  - Dipayan Paul

- Access Laser
  - Yong Zhang

Thank you!
Appendix

– Gantt Chart
– Bibliography
### Gantt Chart

#### Year 1

**Task 1.0** - Project Management, Planning, and Reporting
- Subtask 1.1 Project Management Plan
- Subtask 1.2 Reporting and Budgets
- Subtask 1.3 Presentation and Briefings
- Subtask 1.4 Final report

**Task 2.0** - Design of the $^{14}C$ Supply Units and Microcartridge Systems for Tracer Injection
- Subtask 2.1 Construction of a filling station
- Subtask 2.2 Design and fabrication of a syringe system to hold dissolved tracer gas
- Subtask 2.3 Design and fabrication of a microcartridge system to hold compressed tracer gas
- Subtask 2.4 Optimization of selected injection system

**Task 3.0** - Laboratory Scale Evaluation of Injection Systems
- Subtask 3.1 Design and Construction of High Pressure Flow System for Mixing
- Subtask 3.2 Testing Supply/Injection System with SF$_6$
- Subtask 3.3 Testing Supply/Injection System with $^{14}$CO$_2$

**Task 4.0** - Development of $^{14}$CO$_2$ Detection System

**Task 5.0** - Field Tests of Developed $^{14}$CO$_2$ Tagging Systems

**Task 6.0** - Hazard and Environmental Analyses

#### Year 2

**Task 1.0** - Project Management, Planning, and Reporting

**Task 2.0** - Design of the $^{14}C$ Supply Units and Microcartridge Systems for Tracer Injection

**Task 3.0** - Laboratory Scale Evaluation of Injection Systems

**Task 4.0** - Development of $^{14}$CO$_2$ Detection System

**Task 5.0** - Field Tests of Developed $^{14}$CO$_2$ Tagging Systems

**Task 6.0** - Hazard and Environmental Analyses

#### Year 3

**Task 1.0** - Project Management, Planning, and Reporting

**Task 2.0** - Design of the $^{14}C$ Supply Units and Microcartridge Systems for Tracer Injection

**Task 3.0** - Laboratory Scale Evaluation of Injection Systems

**Task 4.0** - Development of $^{14}$CO$_2$ Detection System

**Task 5.0** - Field Tests of Developed $^{14}$CO$_2$ Tagging Systems

**Task 6.0** - Hazard and Environmental Analyses
Bibliography

• **Journal articles:**