Radiocarbon as a Reactive Tracer for Tracking Permanent CO₂ Storage in Basaltic Rocks

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Presentation Outline

- Benefit to the Program
- Project Overview
- Technical Status
- Conservative and Reactive Tracer Techniques
- Accomplishments to Date
- Summary

Benefit to the Program

 The goal of the project is to develop and test novel geochemical tracer techniques for quantitative monitoring, verification and accounting of stored CO₂. These techniques contribute to the Carbon Storage Program's effort of ensuring 99% storage permanence.

Benefit to the Program cont.

• This research project is developing and testing the feasibility of carbon-14 (14C) as a reactive tracer for quantitative monitoring and accounting of geological CO₂ storage. None of the currently applied CO_2 monitoring approaches are able to provide a surveying tool for **dissolved** or chemically transformed CO₂. The technology, when successfully demonstrated, will provide an improvement over current monitoring practices. This technology contributes to the Carbon Storage Program's effort of ensuring 99% CO₂ storage permanence in the injection zone.

Project Overview: Goals and Objectives

- Testing carbon-14 (¹⁴C) as a reactive tracer for geochemical reactions (including mineral carbonation) caused by CO₂ injection at the CarbFix pilot injection site, Iceland.
- Monitor subsurface CO₂ transport with trifluormethylsulphur pentafluoride (SF₅CF₃) and sulfurhexafluoride (SF₆).
- Drilling small diameter coreholes into injection zone for mineral carbonation study on core samples.
- Quantify the extent of mineral carbonation in the CarbFix basalt CO₂ storage reservoir.
- This research leads to advanced monitoring and accounting of geologic CO₂ storage.

Project Overview: Success criteria

- Complete collection and analysis of fluid and gas samples for ¹⁴C and $\delta^{13}C_{DIC}$ analysis under reservoir conditions in the injection and monitoring wells.
- Complete collection and analysis of fluid and gas samples for SF₅CF₃ and SF₆ analysis under reservoir conditions in the injection and monitoring wells.
- Complete set of breakthrough curves established for monitoring wells.
- Successful drilling of small diameter wells and core recovery at injection reservoir depth with wireline coring.
- Complete quantitative characterization of CO₂-rock reactions caused by CO₂ injection. Determination of in situ mineralization rates.

Technical Status – CarbFix Project



- In situ CO₂ mineralization in basaltic rocks
- Advanced monitoring, verification and accounting of stored CO₂

Groundwater

Target zone for CO₂ sequestration identified at 400-800 m depth

> Gas injected fully dissolved in water into target zone

2 kg/s of CO₂ from Condensers 0.07 kg/s 2.2 thousand tons per year

800 kg/s of steam, gas and water from deep and hot (>240 °C) geothermal wells

Hellisheidi geothermal power plant

Sigfús Már Pétursson

CarbFix Partners

- Orkuveita Reykjavikur (Reykjavik Energy), Iceland
- University of Iceland, Iceland
- CNRS, University of Toulouse, France
- Columbia University, New York, USA

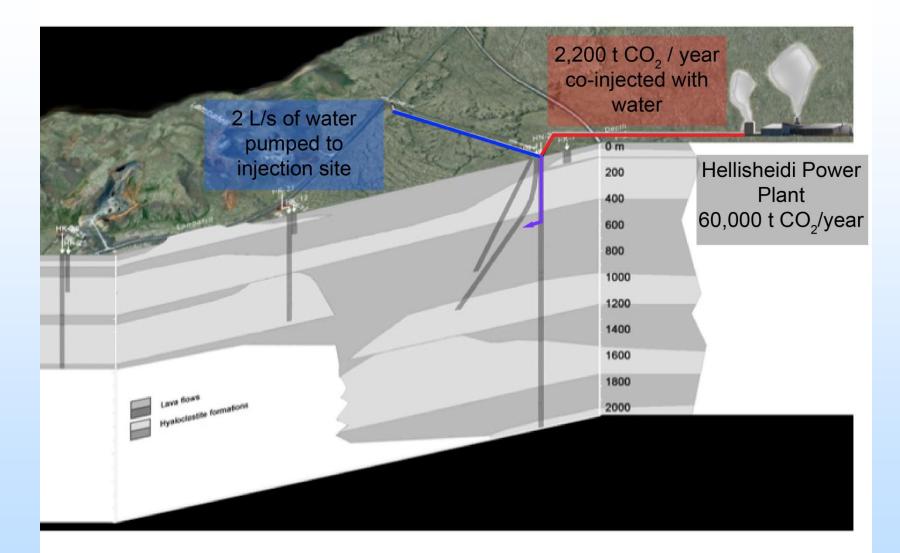
Injection Phases

Phase I pure CO₂ injection of ~200 tons (January 2012- March 2012)

Phase II

 CO_2+H_2S injection (80% CO_2 , 20% H_2S) 1800 tons of CO_2 , (June 2012 – ?)

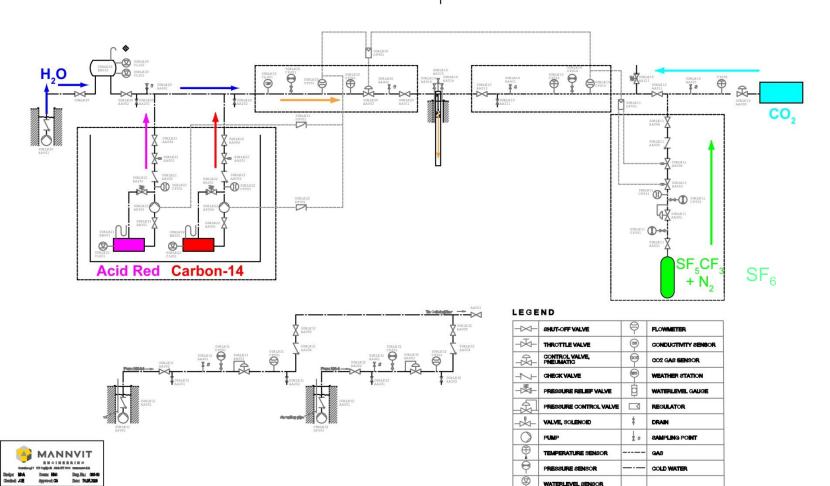
Injection Process



Alfredsson et al. (2012)

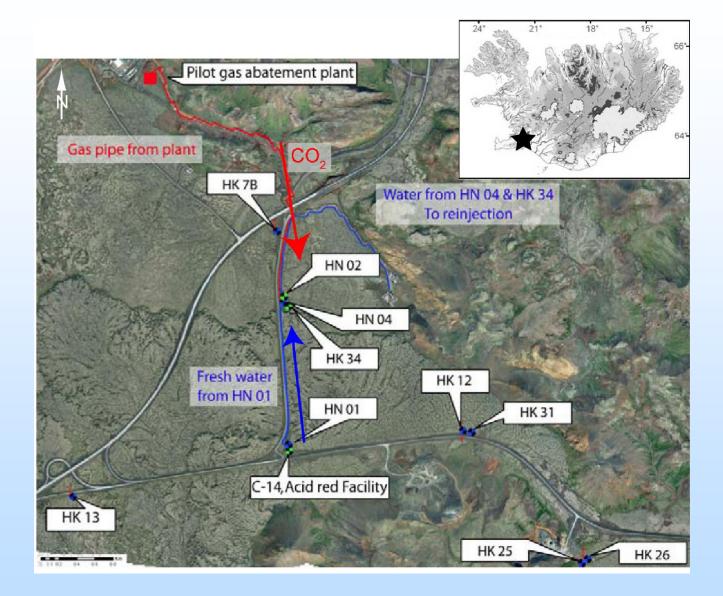
Monitoring/Verification Approach





WATERLEVEL SENSOR

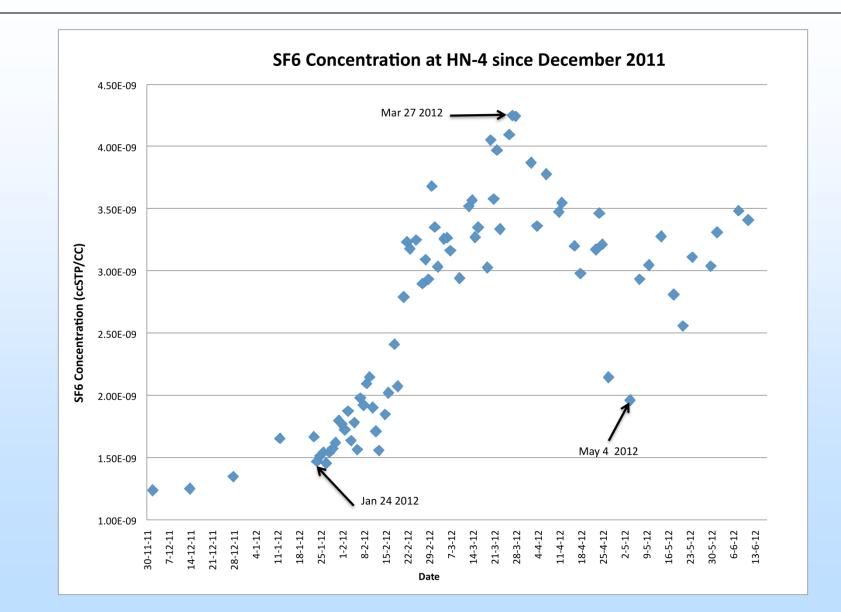
Monitoring/Verification Infrastructure



SF₆ Monitoring Results

- Goal: Monitor advective and dispersive transport
 of injected solution
- Labeling injected CO₂ with SF₆ in Phase I
- Breakthrough curve at HN4 initial peak after 63 days
- Decrease in concentration for a further 38 days
- Continue to monitor SF₆ throughout and beyond Phase II
- No SF₆ at HK-34 or other wells
- Sample analysis with gas chromatography

SF₆ Monitoring Results cont.



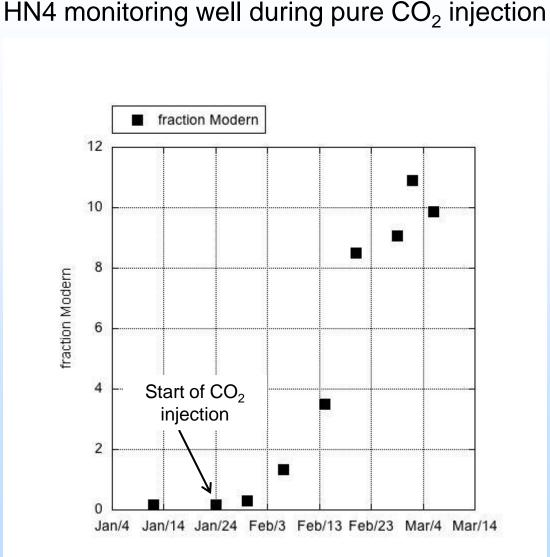
Carbon-14 Monitoring

- Goal: distinguish stored CO₂ from natural CO₂ sources
- Labeling injected CO₂ with carbon isotopic tracer:

$$^{12}CO_2 \rightarrow {}^{14}CO_2$$

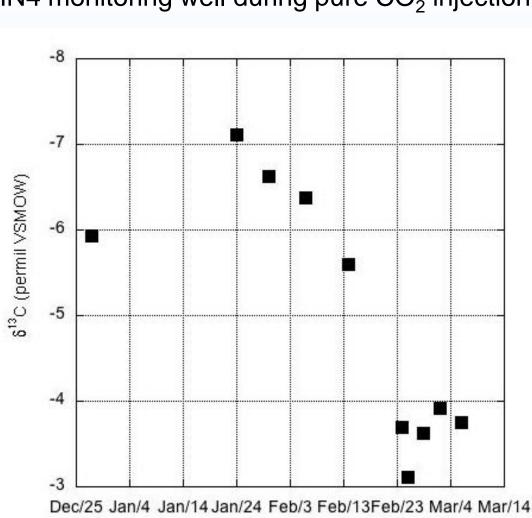
- NaH¹⁴CO₃ stock solution for labeling with an ¹⁴C activity of 20 mCi (7.4x10⁸ Bq) for 12 months injection
- ¹⁴C activity in injected CO₂ saturated solution is 320 PicoCi/L (12 Bq/L)
- Sample analysis with accelerator mass spectrometry

Carbon-14 Monitoring



- Input concentration of ¹⁴C tracer in the injection well was 6 x too high due to a malfunction of the tracer input microprocessor pump.
- ¹⁴C in fraction modern in HN4 monitoring well is 2 x too high.
- Tracer microprocessor pump was replaced and successful ¹⁴C labeling is ongoing.

δ^{13} C Monitoring



- HN4 monitoring well during pure CO₂ injection
- Trend to less negative δ^{13} C values indicate CO_2 -rock reactions (calcite dissolution)
- We need more geochemical data from the injection and monitoring wells to quantify the degree of these reactions.

Accomplishments to Date

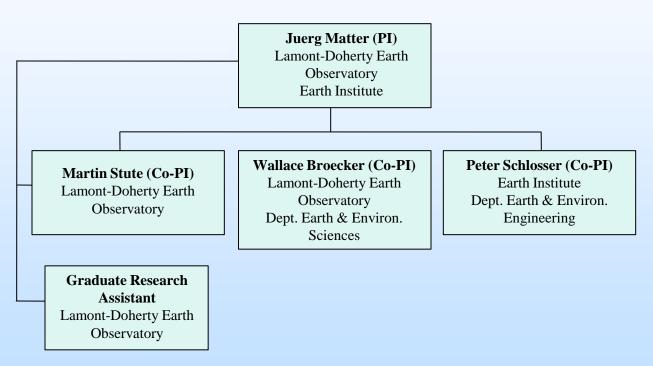
- Tracer injection and monitoring infrastructure including monitoring plan established.
- Pure CO₂ injection completed.
- Continuous sampling in injection and monitoring wells for tracer analysis was initiated.
- First set of gas and fluid samples for SF₆, ¹⁴C and δ^{13} C analysis collected and analyzed.
- $CO_2 + H_2S$ injection was initiated.
- Monitoring the CO₂ + H₂S injection with SF₅CF₃, ¹⁴C and δ^{13} C was initiated.
- The developed technology has the capability to detect and quantify in situ geochemical reactions (see tracer breakthrough curves).

Summary

- Currently injecting gas from the power plant
- Successful and ongoing collection and analysis of tracer samples
- Observed breakthrough curves
- Identified that reactions are occurring
- Next Steps:
 - Continuation of Phase II injection
 - Continuation monitoring through SF₆, SF₅CF_{3, 14}C and $\delta^{13}C$ analysis
 - Plan drilling of well for core samples
 - Quantify CO₂-water-rock reactions

Appendix

Organization Chart



Gantt Chart

Tasks	BP I					BP II				BP III			
	Qt1	Qt2	Qt3	Qt4	Qtr5	Qtl	Qt2	Qt3	Qt4	Qtl	Qt2	Qt3	Qt4
Task 1.0 Project Management, Planning and Reporting													
Task 2.0 Monitoring the CO ₂ movement with SF ₅ CF ₃ in the basalt formation							E						
Subtask 2.1 Monitoring the SF ₃ CF ₃ concentration in target injection interval and overlying shallow aquifer		Α						F		I			
Subtask 2.2 SF ₅ CF ₃ Data Analysis			С					G		Ι			
Task 3.0 Monitoring of geochemical reactions and in situ mineral carbonation with ¹⁴ C							E						
Subtask 3.1 Monitoring the ¹⁴ C concentration in target injection interval and overlying shallow aquifer			в					F		I			
Subtask 3.2 Carbon-14 and d ¹³ C Analysis					D			G		Ι			
Task 4.0 Mineral carbonation studies on core samples													
Subtask 4.1 Wireline core drilling Subtask 4.1.1 Drilling plan								Н		J			
Subtask 4.1.2 Drilling and coring													
Subtask 4.2 Mineralogical and geochemical analysis of core samples												K	
Task 5.0 Quantification of mineral carbonation in the CarbFix basalt storage reservoir												L	