

MONITORING, VERIFICATION AND ACCOUNTING OF GROUNDWATER SYSTEMS ASSOCIATED WITH STORED CARBON DIOXIDE AT GEOLOGIC SEQUESTRATION SITES

BACKGROUND

Safe and effective deployment of geologic carbon storage technology requires assurance that injected carbon dioxide (CO₂) stays in the target storage formation and has no environmental impact on overlying groundwaters. Diverse methods devoted to monitoring, verification and accounting (MVA) activities associated with geologic sequestration are important for helping to protect human health and the environment, preserve sources of drinking water and monitor the integrity of CO₂ storage sites over time. Novel MVA approaches are needed to rapidly identify potential CO₂ and brine leaks at their inception, when mitigation strategies could limit impacts in overlying groundwaters. The methods deployed for use in MVA must be rapid, sensitive and inexpensive for widespread and effective use. A wide range of tools must be available to evaluate the viability of various techniques under changing geologic conditions.



NATIONAL **ENERGY** TECHNOLOGY LABORATORY

PROJECT DESCRIPTION

The National Energy Technology Laboratory (NETL) conducts research on several novel and practical methods for the rapid detection of unintended CO₂ and brine migration into overlying groundwater at geologic CO₂ storage sites. These currently include the advanced geochemical and isotopic analysis of collected water samples; the development of predictive statistical models that identify priority parameters for carbon storage monitoring; and the determination of geochemical processes and measurable signals diagnostic of leakage pathways.

PROJECT GOAL

This project develops and tests new tools and methods for the rapid detection of potential CO₂ and brine leaks into groundwater systems from CO₂ storage sites.

OBJECTIVES

- Develop a suite of geochemical methods and analysis tools for novel groundwater monitoring strategies in geologic storage systems.
- Develop a statistical understanding of natural background variability in CO₂ storage sites.
- Demonstrate the accuracy and robustness of developed tools under field conditions at CO₂ storage and natural analog sites

CAPABILITIES

This project utilizes the following: state-of-the-art geochemical and isotopic analytical facilities; NETL scientists' expertise in aqueous geochemistry; field sampling; and geochemical and statistical modeling.

BENEFITS

The development of rapid and effective methods to determine potential CO₂/brine leakage from geologic CO₂ sequestration sites will help to build confidence in the safety of CO₂ storage and will be useful by operators to demonstrate system conformance. The NETL technologies focus both on rapid screening in water and on more advanced isotopic tools that allow for understanding of chemical reactions signaling potential leakage sources and pathways, providing potentially actionable information to stakeholders.

RECENT ACCOMPLISHMENTS

Development of Novel High-Throughput Methods for Ion and Metal Isotope Measurements in Brines

The NETL research team successfully developed high-throughput and novel methods for accurately measuring ion and metal isotopes in brines affected by CO₂ injection. These brines have high total dissolved solid (TDS) concentrations, which make them challenging to accurately analyze. NETL has developed methods to rapidly analyze these high TDS field samples for ion concentrations that when analyzed, can

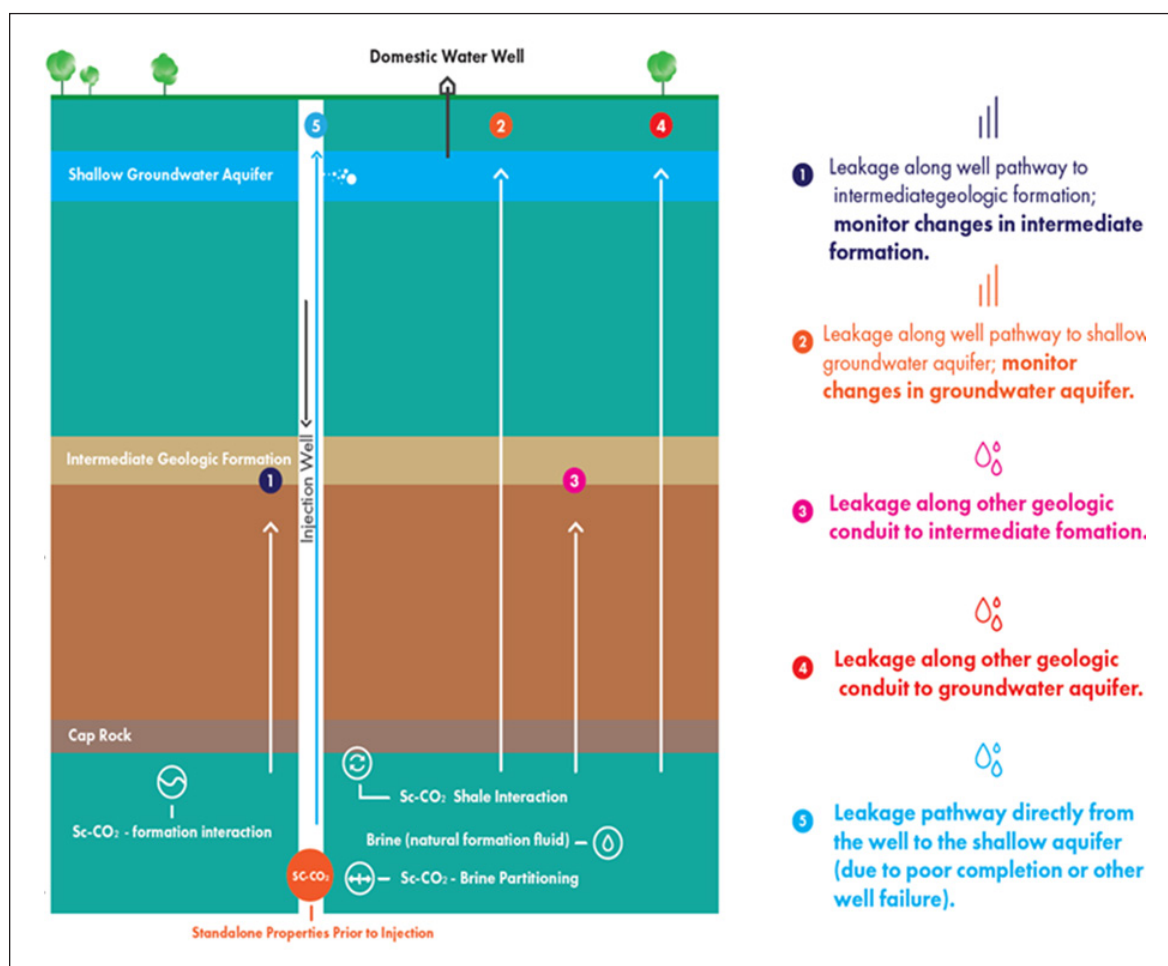


FIGURE 1. Schematic illustrating different CO₂ leakage pathways into overlying groundwaters.

suggest important CO₂-water-rock interactions. Additionally, NETL has developed procedures for tracer analysis, to include: strontium; lithium; uranium and boron isotope measurement in brine; groundwater and rocks using clean-lab chromatographic separation procedures; and NETL's Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS).

These methods are being applied to samples collected at NETL's field monitoring sites throughout the country. Aqueous geochemical and isotopic signals have been used to characterize pre- and post-injection brines and overlying groundwater at an active CO₂ injection site related to enhanced oil recovery (EOR). Fundamental controls on water chemistry in this system prior to and following CO₂ injection are being investigated. Published results indicate that there was no CO₂ induced brine leakage into overlying groundwaters, and that the integrity of the producing formation was maintained during five years of CO₂ injection. NETL researchers identified a suite of inexpensive and effective ion parameters that would indicate CO₂ induced brine leakage in the event of a hypothetical leak. None of these parameters displayed evidence of such leakage during the five-year monitoring study. NETL researchers additionally identified data transformation techniques that made these parameters more sensitive and transformed them into a source attribution tool that could aide in distinguishing between various groundwater salinization sources, such as CO₂-EOR operations, agricultural activity or cross-formational flow.

At the cutting edge of MVA method development, NETL researchers have used several naturally occurring stable isotopes as tools to identify complicated geologic interactions in CO₂ storage related environments. Lithium isotope results, for example, indicate that these measurements would show early indication of potential brine migration into deep groundwater

Natural Analogue Sites

NETL researchers have also applied isotopic geochemical tools at natural analogue sites, which are locations where upwelling CO₂ affects groundwaters. Using strontium, uranium, and carbon isotope data, NETL researchers were able to identify groundwaters affected by two CO₂ transport mechanisms: (1) gas phase CO₂ and (2) CO₂ dissolved in brine. These CO₂ transport mechanisms had different impacts on local groundwater, and identifying the transport mechanism could help mitigation efforts in the case of a leakage event.

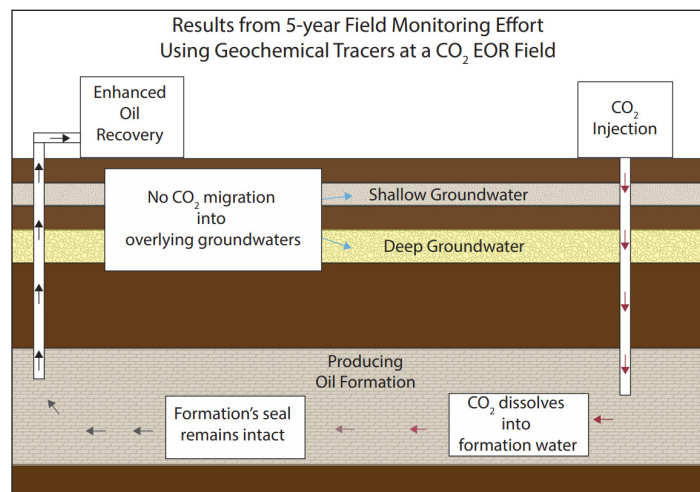


FIGURE 2. Graphical abstract that illustrates primary conclusions from geochemical tracer work at CO₂ EOR field over 5-year monitoring effort.

Using Geochemical and Statistical Models to Predict Leakage Signals and Understand Leakage Detectability

Based on field monitoring work, researchers are now developing geochemical and statistical tools that demonstrate the processes and signals involved in hypothetical leakage scenarios. These models will demonstrate how to monitor for leakage events using the most sensitive geochemical tools depending on the aquifer and fluid characteristics. Using these geochemical model results, the statistical model captures the causal relationship between upstream nodes (CO₂ concentration, geologic formation) and downstream nodes (groundwater parameter changes). This statistical model identifies priority parameters using this probabilistic approach.

PRIOR ACCOMPLISHMENTS

Direct CO₂ Measurement Tools Applied in the Field

A volumetric expansion method used by the carbonated beverage industry and non-dispersive infrared (NDIR) CO₂ sensors adapted for use in water were tested extensively in NETL laboratories. These methods have been used successfully in the field to detect and directly measure CO₂ concentrations in groundwater pumped to the surface at a storage site in Illinois and at an EOR site in Texas.

Integrating Geochemical Model and Statistical Model

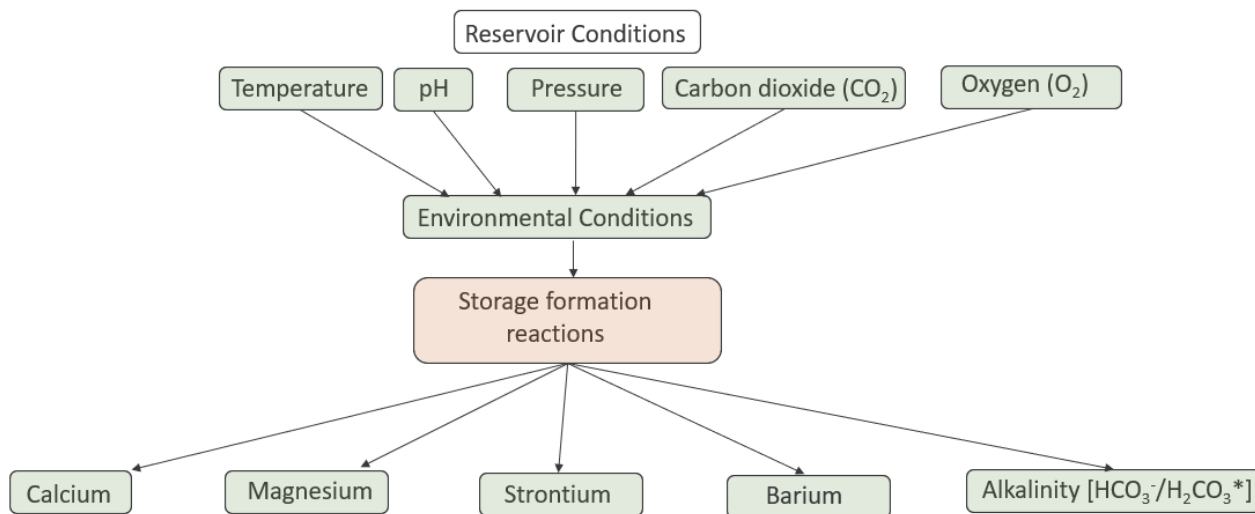


FIGURE 3. Model framework that displays integration of geochemical model output with statistical modeling of sensitive parameters.

Direct CO₂ Measurement Tools Applied in the Field

A volumetric expansion method used by the carbonated beverage industry and non-dispersive infrared (NDIR) CO₂ sensors adapted for use in water were tested extensively in NETL laboratories. These methods have been used successfully in the field to detect and directly measure CO₂ concentrations in groundwater pumped to the surface at a storage site in Illinois and at an EOR site in Texas.

NETL-Developed Sorbent Tubes for Novel PFT for Soil Gas Monitoring

NETL analysis was conducted to support field CO₂ injection projects. In these studies, various perfluorocarbon tracers (PFTs) were added to the CO₂ injection stream at the wellhead. Concurrently, novel gas-permeable glass tubes filled with

Ambersorb® adsorbent were deployed in the soils near the surface and monitored to track if CO₂ leakage occurred. The tubes were then retrieved for analysis using NETL's thermal desorption with cryogenic focusing gas chromatography/mass spectrometry with chemical ionization and selected ion monitoring. PFTs can be measured down to 200 parts per quadrillion.

In-Situ Sensing Technologies

NETL researchers developed a series of novel in-situ analysis tools for detection of CO₂, pH and bulk water chemistry for future down-hole sensing. These include the development of miniaturized laser-induced breakdown spectroscopy (LIBS) sensing devices that will allow for in-situ, real-time analysis of changes in water chemistry, and novel nano-material coatings for fiber optic downhole lines that are engineered to detect CO₂ and/or pH fluctuations at harsh field conditions (elevated temperature and pressure).

Partners

Leidos Research Support Team (LRST)
University of Pittsburgh
Oak Ridge Institute for Science and Education (ORISE)
Mickey Leland Energy Fellows

Contacts

J. Alexandra Hakala
Principal Investigator
Research Physical Scientist
alexandra.hakala@netl.doe.gov

Christina Lopano
Technical Coordinator
Research Physical Scientist
christina.lopano@netl.doe.gov

Dirk Link
Supervisor, Geochemistry Team
Geological & Environmental Systems Directorate
dirk.link@netl.doe.gov

James Gardiner
Primary Researcher
james.gardiner@netl.doe.gov

Burt Thomas
Primary Researcher
randal.thomas@netl.doe.gov