the ENERGY lab

PROJECT FACTS

Carbon Storage – ARRA - GSRA

Molecular Simulation of Dissolved Inorganic Carbons for Underground Brine CO_2 Sequestration

Background

The overall goal of the Department of Energy's (DOE) Carbon Storage Program is to develop and advance technologies that will significantly improve the effectiveness of geologic carbon storage, reduce the cost of implementation, and prepare for widespread commercial deployment between 2020 and 2030. Research conducted to develop these technologies will ensure safe and permanent storage of carbon dioxide (CO_2) to reduce greenhouse gas (GHG) emissions without adversely affecting energy use or hindering economic growth.

Geologic carbon storage involves the injection of CO_2 into underground formations that have the ability to securely contain the CO_2 permanently. Technologies being developed for geologic carbon storage are focused on five storage types: oil and gas reservoirs, saline formations, unmineable coal seams, basalts, and organic-rich shales. Technologies being developed will work towards meeting carbon storage programmatic goals of (1) estimating CO_2 storage capacity +/- 30 percent in geologic formations; (2) ensuring 99 percent storage permanence; (3) improving efficiency of storage operations; and (4) developing Best Practices Manuals. Developing and deploying these technologies on a large scale will require a significantly expanded workforce trained in various carbon capture and storage (CCS) technical and non-technical disciplines that are currently under-represented in the United States. Education and training activities are needed to develop a future generation of geologists, scientists, and engineers who possess the skills required for implementing and deploying CCS technologies.

The National Energy Technology Laboratory (NETL), through funding provided by the American Recovery and Reinvestment Act (ARRA) of 2009, manages 43 projects that received more than $12.7 million in funding that focus on conducting geologic storage training and support fundamental research projects for graduate and undergraduate students throughout the United States. The training and projects can be categorized under one or more of the DOE Carbon Storage Program's five Technology Areas: (1) Geologic Storage and Simulation and Risk Assessment (GSRA), (2) Monitoring, Verification, Accounting (MVA) and Assessment, (3) CO_2 Use and Re-Use, (4) Regional Carbon Sequestration Partnerships (RCSP), and (5) Focus Area for Sequestration Science. This project developed techniques to measure inorganic carbon species in situ.

Project Description

California Institute of Technology (CIT) addressed the need to measure (in situ) the dissolved inorganic carbon (DIC) in underground brine water at higher sensitivity, lower cost, higher frequency, and over longer periods of time as compared to other

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PARTNERS

none

PROJECT DURATION

Start Date 12/01/2009

End Date 11/30/2012

COST

Total Project Value
$300,000

DOE/Non-DOE Share
$300,000 / $0

PROJECT NUMBER

DE-FE0002057

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MVA efforts for the geologic storage of CO_2. The use of Quantum Cascade Lasers (QCLs) to provide mid-range infrared (IR) spectroscopic measurement can provide a means to quantify the mass of CO_2 stored in a geologic storage formation as a function of time. CIT performed the quantum mechanics (QM) electronic structure calculation on DIC species (e.g., CO_2, bicarbonate ion (HCO_3-), and carbonate ion [CO_3^{2}-]) to accurately describe the physical carbon storage system. QM is a set of scientific principles that describe the known behavior of energy and matter at atomic and subatomic scales. Electronic structure calculation is a computational approach that can be used to determine the atomic structure of a material and its electronic properties. The QM results were used to perform a molecular simulation of the DIC species mid-infrared (MIR) spectra at the high-temperatures and pressures representative of carbon storage conditions. From this simulation, the full MIR spectra were evaluated using the perturbation theory (a mathematical method to find an approximate solution to a problem that cannot be directly solved under high-pressure, temperature, and differing pH conditions). The final research simulation results include the MIR spectra of DIC species and chemistry at real brine conditions (i.e., high salinity, pressure, and temperature).

Goals/Objectives

The project contributed to the advancement of carbon storage MVA techniques by evaluating better, more efficient ways to measure inorganic carbon in situ. This research advanced efforts to track and ensure storage permanence of injected CO_2. Specific project objectives include:

- Use first principles QM and ReaxFF (a reactive force field simulation used for molecular dynamic simulations) to predict the MIR spectra of DIC species in water.
- Determine how the MIR spectra change with external conditions (temperature, pressure, salinity).

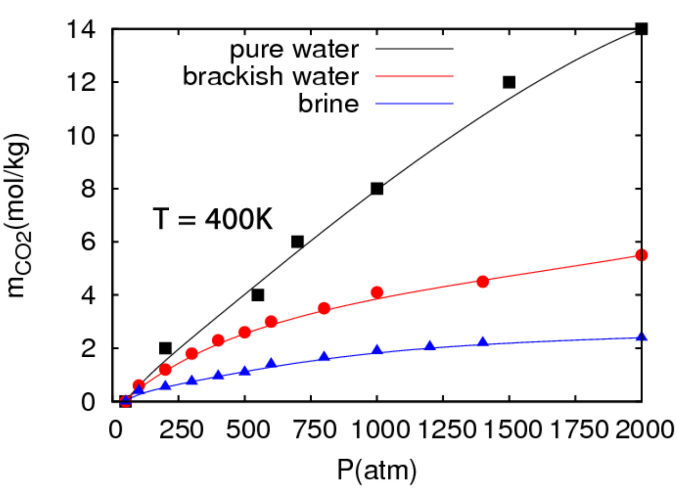

Figure 1. Calculation of CO_2 storage in brine assuming no conversion of CO_2 to HCO_3-.

- Determine the acidity changes as a result of pressure, temperature and the presence of supercritical CO_2 during underground brine water carbon storage process.
- Provide graduate students and scientists professional training in molecular simulation to prepare them for the applications of the acquired knowledge for carbon storage.

Accomplishments

- By the completion of the project, nine personnel had accumulated 6,807 training-related hours under the program.
- The project team monitored the change in the population of the relative DIC species as a function of time over varying temperatures, pressures, and salinity concentrations. The major results include: 1) Carbon dioxide is the preferred species of DICs with increasing temperature and pressure, suggesting that a substantial amount of CO_2 can be stored in brine in the subsurface; 2) solvated CO_2 molecules exist predominately as CO_2-H_2O motifs in solution; 3) linear response theory can successfully allow researchers to efficiently calculate the experimental IR spectra of DICs under various temperature and pressure conditions, with excellent agreement with laboratory experiments.
- Recognizing changes to the population of DIC species under a variety of conditions encountered in a laboratory setting can be used to further identify the presence of CO_2 in the subsurface as a variety of species in a geologic storage application.
- The project team advanced the simulation of DICs under pure water, salty water, and brine conditions at high temperature and pressure. Results shows that the CO_2 species are preferentially stabilized by the brine over the HCO_3- species even more than previously found in pure water. The team observed a 25 percent enrichment of CO_2 relative to HCO_3- at 350 °K and 25GPa in pure water, a 33 percent enrichment in brackish water (0.5M NaCl concentration) and a 47 percent enhancement in brine (5.5M NaCl concentration).
- A final report has been completed and is now available.

Benefits

Overall, project research contributed to the design of a QCL spectrometer that can be used to monitor carbon storage sites with higher sensitivity of DIC measurement. This type of technique helps to quantify and resolve DIC at high sensitivity over extended spatial scales, will improve the reliability of next-generation detection and sensing technologies, and can be used to quantify the mass of stored CO_2. This research helps to meet the Carbon Storage Program's goal of developing technologies to ensure 99 percent storage permanence. Through the research, students were trained with state-of-the-art molecular simulation tools and capabilities that are preparing them to further develop carbon storage technologies necessary for future commercial-scale CCS.