

Linking the Chemical and Physical Effects of CO₂ Injection to Geophysical Parameters

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Abstract

The proposed research aims to demonstrate techniques for quantitatively predicting the combined seismic signatures of CO₂ saturation, chemical changes to the rock frame, and pore pressure. This will be accomplished (i) by providing a better understanding the reaction kinetics of CO₂-bearing reactive fluids with rock-forming minerals, and (ii) by quantifying how the resulting long-term, CO₂-injection-induced changes to *the rock pore space and frame* (e.g. porosity, permeability, mineral dissolution, and cementation) *affect seismic parameters in the reservoir*.

This research will involve laboratory, theoretical, and computational tasks in the fields of both Rock Physics and Geochemistry. Samples will be selected based on mineralogy (carbonates, sandstones, and calcite-cemented sandstones), porosity, pore and cement type. Ultrasonic P- and S-wave velocities will be measured over a range of confining pressures while injecting CO₂ and brine into the samples. Pore fluid pressure will be varied and monitored together with porosity during injection. The measurement of rock physics properties will be integrated and complemented by those obtained via geochemical experiments to link the physical (e.g. porosity enhancement, selective dissolution and change in microstructure) and chemical processes (e.g. reaction type and dissolution rates) underlying the mechanisms triggered by CO₂ injection. Our original proposal, approved by GCEP, was to include a subcontract to Texas A&M University for laboratory measurements and analysis to be made by Prof. John Morse. The measurements were aimed at determining CO₂-related dissolution rates of carbonate-bearing rocks over a range of pressures. Due to the untimely death of Dr. Morse in December, 2009, we find it necessary and desirable to move the work to Rice University, to be performed by Prof. Andreas Luttge and Dr. Rolf Arvidson. Analysis of reaction rate during crystal growth, dissolution, oxidation, hydration, etc. will be made by using Vertical-Scanning-Microscopy (VSM) that allows imaging of the dissolution process at the molecular scale. In particular, the analysis will be made through comparison of VSI digital height maps of surface topography as a function of time. Results will provide the requisite data for modeling the acoustic response of dissolution. Flow-through

experiments on rock plugs upon measurements of the acoustic properties along with CT-scan imaging will be made to quantify and image changes to the host rock pore structure and permeability due to dissolution and precipitation reactions. We will also develop computational and analysis tools needed to simulate multi-fluid flow at the pore scale while including dissolution effects. We will use single- and two-phase Lattice-Boltzmann flow simulation and diffusion simulation to model CO₂ sequestration on a sample scale in 3D.

The innovation will be in using experimental data and models from geochemistry and rock physics to quantify the seismic signatures of the physicochemical processes occurring during CO₂ injection. The deliverables will be an innovative dataset, methodologies, and algorithms for predicting the seismic response of multiphase flow and reactions in CO₂ storage programs. These deliverables will provide essential fundamentals for quantitative sequestration monitoring.

Introduction:

Monitoring, verification, and accounting (MVA) of CO₂ fate are three fundamental needs in geological sequestration. The primary objective of MVA protocols is to identify and quantify (1) the injected CO₂ stream within the injection/storage horizon and (2) any leakage of sequestered gas from the injection horizon, providing public assurance. Thus, the success of MVA protocols based on seismic prospecting depends on having robust methodologies for *detecting* the amount of change in the elastic rock property, *assessing* the *repeatability* of measured changes, and *interpreting and analyzing* the detected changes to make quantitative predictions of the movement, presence, and permanence of CO₂ storage, including leakage from the intended storage location. This proposal addresses the problem of how to interpret and analyze the detected seismic changes so that quantitative predictions of CO₂ movement and saturation can be made. The main goals are:

- (a) linking the chemical and the physical changes occurring in the rock samples upon injection;
- (b) assessing the type and magnitude of reductions caused by rock-fluid interactions at the grain/pore scale;
- (c) providing the basis for CO₂-optimized physical-chemical models involving frame substitution schemes.

Background:

Having the appropriate rock-physics model is generally a key element for time-lapse seismic monitoring, both to infer the significance of detectable changes (*i.e.* qualitative interpretation) and to convert them into actual properties of the reservoir rocks (*i.e.* quantitative interpretation). Nevertheless, because of the peculiar ability of CO₂-rich water to promote physicochemical imbalances within the rock, we must address whether traditional rock-physics models can be used to invert the changes in geophysical measurements induced in porous reservoirs by the injection of CO₂, making it possible to ascribe such changes to the presence or upward migration of CO₂ plumes. Making this determination requires an understanding of the seismic response of CO₂-water-rock

systems. Seismic reservoir monitoring has traditionally treated the changes in the reservoir rock as a physical-mechanical problem—that is, changes in seismic signatures are mostly modeled as functions of saturation and stress variations (*e.g.* pore and overburden pressure) and/or intrinsic rock properties (*e.g.* mineralogy, clay content, cementation, diagenesis...). Specifically, modeling of fluid effects on seismic data has been based almost exclusively on Gassmann's equations, which describe the interaction of fluid compressibility with the elastic rock frame to determine the overall elastic behavior of rock. Beginning with the bulk (K_s) and shear (μ_s) moduli of the mineral composing the rock, we use Gassmann's fluid substitution scheme to compute the bulk modulus of the saturated rock (K_{sat}) from the bulk modulus of the fluid (K_{fl}) and from that of dry rock (K_{dry}). However, depending on the properties of the mineral composing the rock and the properties of the fluid, complex rock-fluid interactions may occur at the pore scale, leading to dissolution and formation of new mineralogical phases. All these physical modifications may compete in changing macroscopic rock properties such as permeability, porosity, and elastic velocities, which, in turn, can change the baseline properties for the Gassmann's fluid substitution scheme. This entails two consequences: (a) a classical fluid-substitution scheme may underpredict time-lapse changes and thus mislead 4D monitoring studies; and (b) predictions of *in situ* velocity will compensate for the chemically softened velocities with erroneous estimates of saturations and/or pore pressure.

Results

The Project Kickoff Meeting was held on January 15, 2010;

We are currently establishing an experimental protocol combining (a) measurements of the geochemical properties (*i.e.*, pH and Calcium content) of the CO₂-rich fluids and their evolution upon injection; (b) measurements of the acoustic properties of the rock samples and their variation upon injection and (c) time-lapse SEM and High resolution microCT imaging to monitor and quantify the changes to the pore space and sample microstructure associated with the injection. Ultrasonic P- and S-wave velocities are measured under confining pressure while injecting CO₂-rich water into the samples. The experimental device consists of a fluid injection system and a core-holder equipped with three linear potentiometers to measure length changes of the sample as a function of stress and with two pairs of piezoelectric transducers for the measurement of P- and S-waves velocities (at 1MHz and 0.7MHz respectively). The sample is jacketed with rubber tubing and inserted into the pressure chamber under a variable confining pressure. So far, experiments have been conducted under pressure conditions of 1.1MPa. The injected fluid is an acidic solution prepared by saturation of deionized water with CO₂. Rates of depletion are set lower than rates on injection, resulting in a flow rate of 4 to 8 mL/min. P- and S-waves velocities were acquired under fully saturation conditions and pore fluid pressure of 1.0MPa. Before proceeding with the next injection, the sample is dried *in* the vessel for about 10h, by alternating the injection of dry and warm air and dry helium. The fluid was regularly sampled at the outlet in order to measure calcium content and total hardness (calcium, magnesium and all other polyvalent ions which can be substituted in the calcite crystal lattice) by a titration method with a digital titrator and

EDTA as titrant. The injected pore volumes are then calculated by dividing the volume of the injected fluid by the initial pore volume of the sample (V_{norm}).

Figure 1 shows the variation of P- and S-waves velocities as a function of the number of injected pore volumes. The plot of Figure 4a also reports the velocity values measured before injection. Solid symbols denote measurements under fully saturated conditions (confining pressure of 1.1MPa and pore fluid pressure of 1.0MPa), open symbols are for *in vessel dry* conditions. Open red symbols describe bench-top velocity values measured after 48h of oven-drying at 70°C. Experimental P- and S-waves velocities, in both dry and fully saturated conditions decrease upon injection showing a steeper decrease during the first stages of the injection experiment.

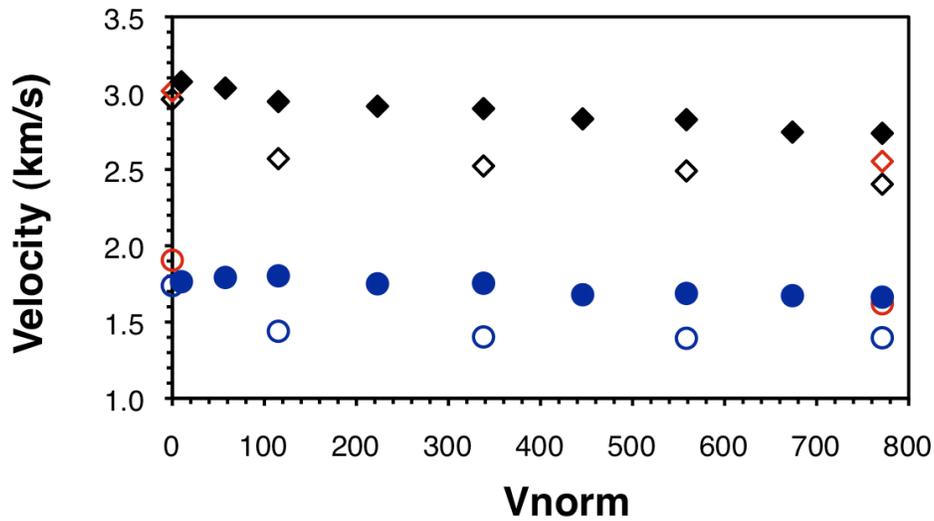


Figure 1: Variation of the measured ultrasonic P- and S-waves velocities, as a function of the injected pore volumes. Open and solid symbols denote respectively dry and saturated conditions.

Figure 2 shows time-lapse SEM (*top*) and High resolution microCT imaging (*bottom*) to monitor and quantify the changes to the pore space and sample microstructure associated with the injection.

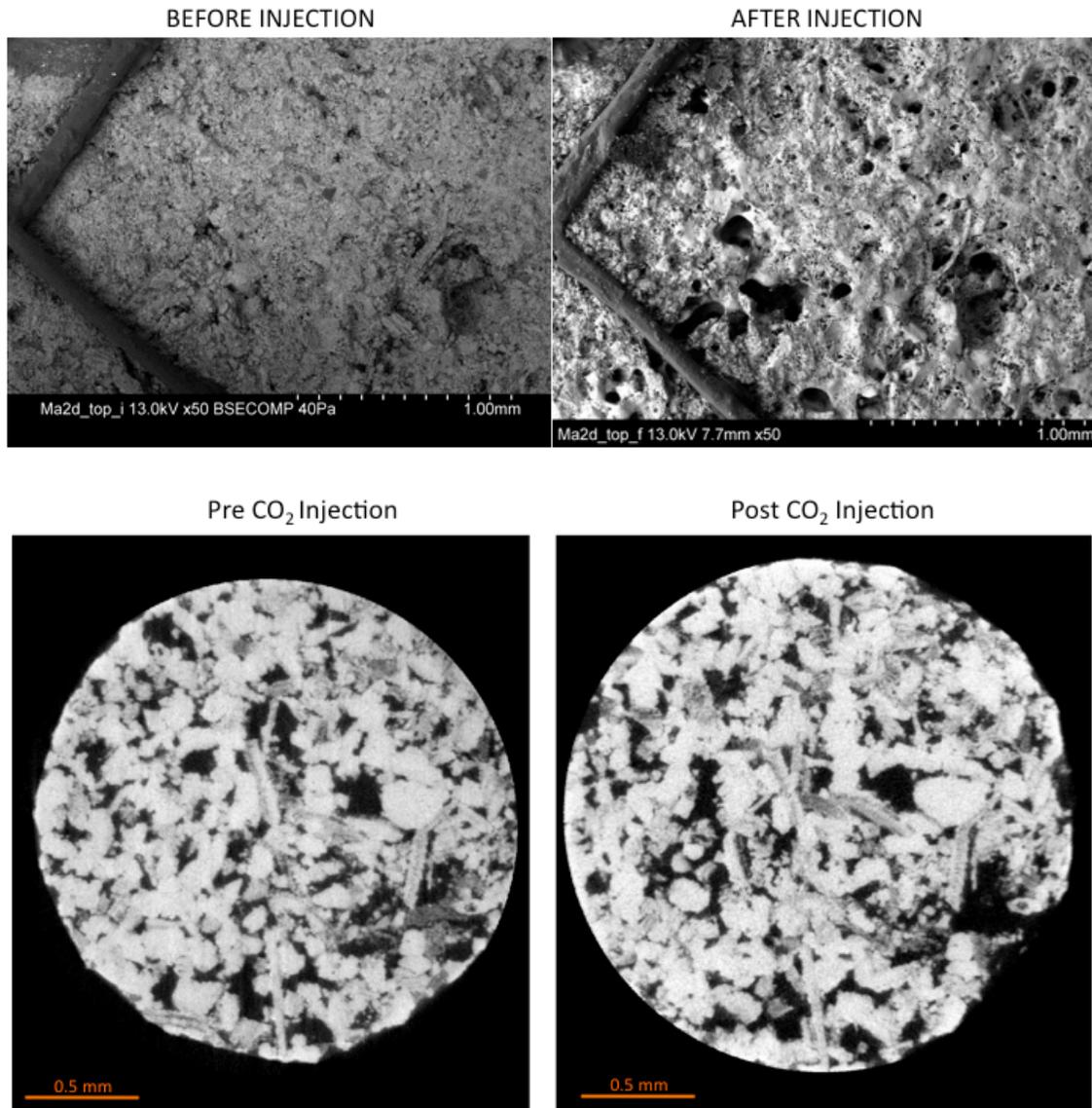


Figure 2: Time-lapse SEM (*top*) and High resolution microCT imaging (*bottom*) to monitor and quantify the changes to the pore space and sample microstructure associated with the injection.

Progress

The interim reliance on fossil fuels makes sequestration of CO₂ in geological formations one of the carbon-management technologies having the potential to substantially reduce greenhouse gas emissions while achieving energy sustainability. To translate such potential into concrete development outcomes, realized benefits, and policy, common concerns (i.e. pore pressures reactivating faults or fractures, risk of leakages, and loss of storage capacity) need to be dispelled. These concerns are thus

intimately associated with our ability to use geophysical techniques to monitor chemical processes and their effects on the rock properties. Exploring the links between geophysical observables, rock physical properties, and geochemical induced long-term changes upon CO₂ sequestration and introducing them into standard monitoring programs are necessary steps to go towards quantitative predictions of pore pressure, saturation, and storage capacity.

The proposed project will be the first comprehensive study aimed at a better fundamental understanding of the geophysical signatures associated to the physicochemical processes occurring upon CO₂ injection. It will provide an essential element for remote probing and tracking of both chemical and physical processes associated with injection of reactive fluids (e.g. CO₂).

Future Plans

Sample collection from other injection-site relevant lithologies is also underway. We made arrangements with the Bureau of Economic Geology, UT Austin to collect samples from the sedimentary logs of the Cranfield injection zone. Cores will be from BEG's monitoring wells (CFU 31F-2 and CFU 31F-3). Acoustic measurements will be performed under higher confining pressure to study the role of crack closure, leading to a lower reactive surface area, on the measured parameters.

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