SUMMARY

Time-lapse seismic monitoring is a widely used method for studying time-evolving processes of the Earth’s subsurface in a wide range of applications (i.e., hydrocarbon production, fluid-migration in tectonically active regions, and environmental engineering). The pivotal concept of this method is that changes in seismic velocity and density depend on the variation of the properties of the rock frame and the fluid permeating it in response to changes of physical parameters such saturation, pore fluid pressure, temperature, and stress. Increasingly, however, time-lapse seismic monitoring is called upon to measure and quantify subsurface changes caused by geochemical processes due to the injection of fluids unlikely to be in chemical equilibrium with the host rocks (i.e., surfactants, CO2, bacterial growth promoters, chemical oxidants).

This paper springs from a series of laboratory experiments and high-resolution images monitoring changes in microstructure, transport, and seismic properties of rock samples when injected with CO2. Results show that CO2 injection into a brine-rock system induces precipitation and dissolution in the host rock, which permanently change the rock frame. These alterations change the baseline transport and elastic properties of the rock frame and thus the input parameters of rock physics models and reservoir simulators.
**Introduction**

4D seismic technology, coupled to rock physics, has emerged as an effective tool to quantitatively characterize the reservoir dynamics associated with hydrocarbon production. Gassmann’s model (Gassmann, 1951) is used as the general basis for interpreting the effect of fluids on both log and seismic velocity data. The model scheme performs a mere fluid substitution treating the rock-fluid interaction as a purely mechanical problem. It is a common practice in the literature to include the time-variant effects on the properties of the fluid and the rock frame due to the variation of physical parameters such as stress and temperature (Nur et al., 1984; Lumley, 2001; Meadows et al., 2005). Nevertheless, data interpretation almost never includes geochemical effects on the properties of the frame. A basic assumption of Gassmann’s theory is, in fact, that the fluid and the rock matrix are at, or close to, chemical equilibrium, and hence they do not interact. However, rock-fluid interactions can be relevant when interpreting changes in the reservoir properties due to the injection of CO₂ for enhanced oil recovery and/or for environmental applications.

A growing body of recent field evidence show that, when CO₂ is injected into reservoirs, the observed time-lapse seismic effects can be greater than those predicted by Gassmann-consistent model schemes. These discrepancies are seen whether the target reservoir is sandstone (Daley et al., 2006), coal (McCrank and Lawton, 2009) or carbonate rocks (Raef et al., 2004; Wang et al., 1998). A few field- (Daley et al., 2006; Wang et al., 1998) and laboratory- studies (Wang et al., 1998) also reported a non-negligible decrease of S-wave velocity upon CO₂ injections in addition to the expected change in P-wave velocity. Several factors can contribute to such a discrepancy, including effects due to pressure-consistent porosity changes (Wang et al., 1998). In addition, though, CO₂ injection induces coupled processes of multiphase fluid flow, interphase mass transfer, chemical reactions, and mechanical deformation leading to formation damage. In brine-saturated formation, CO₂ injection induces formation dry-out leading to precipitation of mineral salts. On the other hand, numerical studies of CO₂ injection showed that up to 29% of the total injected amount would dissolve into formation water, causing interactions between the formation water, the CO₂, and the rock that will strongly depend upon the thermodynamic conditions, the mineral assemblage, the initial composition of the formation water, and the hydrodynamic regime. Hovorka (2009) reported that at Frío part of the CO₂ dissolved rapidly into brine, causing pH to fall and calcite to dissolve. In addition, large amounts of iron (Fe) and manganese (Mn) were also dissolved in the initial fluids as the CO₂ front moved though the rock-water system.

This paper addresses the effect on time-lapse seismic and transport data due to permanent changes in the rock matrix, such as precipitation and dissolution processes induced by injection of CO₂. The main purpose of this work is to show the need to extend the current rock-physics toolkit for analyzing chemical and physical coupling between reactive pore fluids and rock matrices. We need 1) laboratory data to assess the relevance of the geochemical effects on the transport and elastic properties and 2) rock physics transforms linking the time-variant effects on the rock frame properties and the site-relevant geochemical process. We present here recent results from our laboratory program at Stanford University showing the magnitude and direction of changes induced in rock porosity and permeability, and the consequent changes in P- and S-wave velocity. To comprehend the mechanisms responsible for the time-lapse changes in the transport and elastic rock properties, we also present high-resolution time-lapse SEM and CT-scan images showing how and where precipitation and dissolution affect rock microstructure.

**Laboratory Experiments and 4D High-Resolution Rock Imaging**

We are conducting several laboratory experiments to investigate the magnitude and direction of changes in rock porosity, permeability, and P- and S-wave velocity induced by precipitation and dissolution processes occurring upon CO₂ injection. Figure 1 shows the amount of porosity and permeability reduction and the consequent increase of P- and S-wave velocity in Fontainebleau sandstones as a result of salt precipitation in the pore microstructure. These rocks encompass a wide spectrum of microstructures, helping us understand the role of microstructure in controlling precipitation. Two different processes induced salt precipitation: (1) evaporation driven by temperature and (2) drying induced by CO₂ injection. The first, most striking result is that the induced
changes in the transport properties fit the variation of the permeability-porosity data of the untreated samples (gray data, Figure 1), following the natural diagenetic trend of these rocks. Secondly, the rate of change seems to be controlled by the initial permeability-porosity value, implying that the initial microstructure greatly influences how the rock and its properties change upon salt precipitation. Figure 2 shows the variation of P- and S-wave velocities as a function of porosity before and after the induced salt precipitation. As with permeability and porosity, the greatest changes in the acoustic properties occur in rock samples characterized by porosity lower than 15%.

![Figure 1](image1.png)

**Figure 1** upper panel- CT-scan images of low, medium, and high porosity-permeability sandstones used in this study, highlighting differences in sample microstructure; lower panel- variation of permeability as a function of porosity for Fontainebleau sandstones measured before (red dots) and after (yellow dots) alternating injection of seawater and CO$_2$ injection. Data describing the natural permeability-porosity diagenetic trend of Fontainebleau sandstones from Gomez et al., 2010 and Bourbie and Zinszner, 1985 are reported for comparison.

![Figure 2](image2.png)

**Figure 2** Variation of P-wave (blue diamonds) and S-wave (red squares) velocities upon induced salt precipitation, as a function of porosity. Open symbols indicate values before precipitation, and solid symbols indicate values after precipitation.

Figure 3 (left panel) shows laboratory measurements published by Vialle and Vanorio (2010) of compressional and shear velocities in carbonate rocks as functions of the injected volume of CO$_2$-rich water. Velocities and injected volumes are normalized with respect to the pre-injection values of velocities and porosity, respectively. Three important facts jump out of these data. First, as fluid volumes are injected, there is a large decrease in both the P- and S-wave velocities (~25% and 21%, respectively) of the saturated (filled symbols) and dry (open symbols) rocks, compared to their pre-
injection values. Decrease in velocity is accompanied by an increase in both porosity and permeability (Vialle and Vanorio, 2010). Second, the observed decrease in velocity of the dry rock frame after a given volume is injected varies among the samples by as much as 25-30% though all velocity data are from rocks composed predominantly of calcite. Third, the decrease of velocity under a constant confining pressure levels off with time, despite increasing the injected volumes. Although changes in the carbonate rock frame were expected because of the dissolution of CO$_2$ into the pore fluid, this observation makes it clear that mineral composition is not the only factor controlling the chemical and physical mechanisms responsible for the observed changes. Figure 3 (right panel) shows the variations of the normalized P- and S-wave velocities of the dry rock frame after injection. Data refer to carbonate samples characterized by similar microcrystalline calcite content (i.e., micrite) (Vanorio and Mavko, 2011) and measured under different conditions of confining pressure: bench-top, 1 MPa, and 8 MPa.

Data show that increasing the confining pressure exerted on the sample decreases the variation in the velocity of the rock frame upon injection. In pressure-sensitive rocks such as chalks, velocity decreases by ~30% during an experiment performed under bench-top conditions, whereas it decreases by only ~10% at 8 MPa. This behavior results from two competing and interdependent processes, which ultimately control the variation of velocity. On the one hand, chemical dissolution of calcite as testified by the increase of Ca in the pore fluid, enhances porosity and softens grain contacts; on the other hand, samples experience a pressure-dependent mechanical compaction driven by dissolution. The higher the pressure, the larger the compaction experienced by the sample, which in turn translates into low-aspect-ratio pore closing and a decrease in the reactive surface area. Ultimately, both compaction and the diminished reactivity curb the rate of velocity decrease with increased injection and/or time.

One important aspect of this research is imaging the dissolution- and the precipitation-induced changes to the pore microstructure to understand the physical and chemical processes governing the changes in the macroscopic properties. Figure 3 shows the effects of (1) salt precipitation in a brine-saturated sandstone (top, left panel) and (2) pore dissolution in a carbonate flushed with CO$_2$-rich water (top, right panel and bottom panel). The figure clearly shows pore clogging due to salt precipitation at the grain contacts and porosity enhancement due to dissolution; both processes are responsible for changing the baseline properties of the rock frame and thus, the input parameters for fluid substitution.

Figure 3 Normalized, ultrasonic P-wave (top) and S-wave (bottom) velocities versus the injected pore volumes of CO$_2$-rich water in carbonate samples. Left panel - Open and solid symbols refer to measurements performed under dry conditions (from Vialle and Vanorio, 2010). Right panel - symbols refer to measurements and injections performed under different conditions of confining pressure: bench-top (squares), 1 MPa (triangles), and 8 MPa (dots). P- and S-wave velocities are normalized with the respect to their pre-injection values.
Figure 3: Time-lapse SEM (top) and CT-scan (bottom, courtesy of Ingrain, Inc., Houston, TX) images monitoring the effect of CO₂ injection on pore microstructure: (top, left panel) induced salt precipitation within sandstones; (top, right panel and bottom panel) induced dissolution within a carbonate rock.

Conclusions

Conventional rock models for seismic signatures of pore-fluid changes are purely mechanical. Hence they may be inadequate for quantifying the effects of injected CO₂-bearing fluids for EOR and sequestration on in-situ seismic velocities. Experimental and imaging data show that the seismic response of CO₂-brine-rock systems is far from being a pure fluid-substitution problem. To take full advantage of advances in fast and high-repetition seismic reservoir monitoring, optimized physicochemical models involving frame-substitution schemes must be developed to account for the types and magnitudes of changes caused by rock-fluid interactions at the grain or pore scale.

References