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**Monitoring, Verification, and Accounting of CO<sub>2</sub> Fate in Geologic Formations: Linking the  
Chemical and Physical Effects of CO<sub>2</sub> Injection to  
Geophysical Parameters**

Tiziana Vanorio and Gary Mavko  
Stanford Rock Physics Laboratory, Stanford University, CA

Monitoring, verification, and accounting (MVA) of CO<sub>2</sub> fate are three fundamental needs in geological sequestration. The primary objective of MVA protocols is to identify and quantify (1) the injected CO<sub>2</sub> 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 depends on having both *instruments that can detect* the presence, movement, and state of carbon in a storage reservoir, including leakage from its intended storage location, and *robust methods for interpreting and analyzing* data from such instruments so that quantitative predictions of the movement, presence, and permanence of storage can be made. Our research addresses this second need.

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...). Experimental and theoretical rock physics have been used to study how changing rock-physical properties affects the response of geophysical observables, thus providing the foundation for quantitative reservoir characterization. However, management and control of multiphase subsurface flow associated with CO<sub>2</sub> injection pose formidable challenges and risks, because rock-CO<sub>2</sub> interactions are not purely mechanical. As a consequence, several pitfalls may arise while geophysically mapping CO<sub>2</sub> distributions, particularly when CO<sub>2</sub> signatures are masked by ambiguities in the scales of CO<sub>2</sub>-water mixing and by chemical changes to the host rock due to dissolution and/or precipitation (change in porosity, changes at the grain contacts, and/or mineral transformation). Conventional models for seismic signatures of pore-fluid changes are purely mechanical and hence inadequate for measuring the effects of CO<sub>2</sub>-bearing reactive fluids on in-situ seismic velocities. Errors from ignoring chemical reactions can affect not only the magnitude, but also the sign, of predicted velocity changes.

Until now, 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. This approach can work well under conditions of single-phase fluid saturation in relatively inert systems, in which the pore fluids and minerals are at, or close to, chemical equilibrium. However, this modeling approach very likely oversimplifies the complex rock-fluid interaction that occurs while injecting CO<sub>2</sub> underground. As a consequence, treating the rock pore space and frame as invariant and basing the computation of the effective compressibility of the fluid-gas system on homogeneous saturation distributions will not correctly map the fate of CO<sub>2</sub>.

Figure 1 shows forward modeling of seismic P- and S-wave velocities ( $V_P$  and  $V_S$ ) in reservoir rocks during  $CO_2$  injection, hypothesizing three end-member scenarios: uniform saturation (red line), patchy saturation (blue line), and porosity enhancement due to dissolution (100% water saturation, green line). Point A (left panel) corresponds to the initial pre-injection  $V_P$  of the water-saturated host rock. An observed  $V_P$  decrease of 100 m/s could correspond to a  $CO_2$  saturation of either ~20% (Point B) if the gas-water saturation is spatially “patchy” (coarse-scale mixing), or <1% (point C), if the gas-water saturation is spatially “uniform” (fine-scale mixing)—a saturation uncertainty of ~20%. Similarly, an observed  $V_P$  decrease of 250 m/s could correspond to  $CO_2$  saturation as high as 40% (point B’) or as low as ~1% (point C’)—an uncertainty of ~40%.

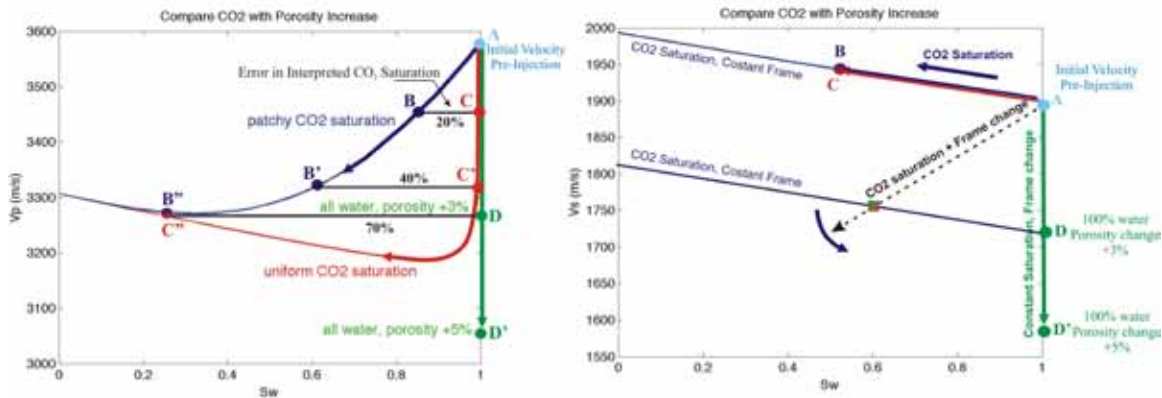


Figure 1. Forward modeling of the P- and S- seismic signatures of rocks during  $CO_2$  injection (top panel). Three scenarios are shown: uniform saturation (red line), patchy saturation (blue line), and porosity enhancement due to dissolution processes (100% water saturation, green lines). The figure also shows the errors in interpreted  $CO_2$  saturations (black labels).

*These examples illustrate a dangerous monitoring pitfall: an observed P-wave velocity anomaly could indicate either a successfully-captured, high-saturation  $CO_2$  plume, or a trace residual saturation remaining after the  $CO_2$  has escaped; failure to incorporate the correct saturation model could lead to drastic monitoring errors.*

Seismic interpretation of  $CO_2$  saturation can be even more complex if we introduce chemical effects. The green arrow in Figure 1 (left) indicates the effect of mineral dissolution on P-wave velocity, in this case with full water saturation (no gas-phase  $CO_2$ ). We now see that a  $V_P$  decrease of 300 m/s could correspond to  $CO_2$  saturation as high as 70% if there is no chemical interaction or as low as zero if there is dissolution. (Note that at  $CO_2$  saturations larger than ~70%, the patchy and uniform curves converge.)

Figure 1 (right panel) shows that the use of S- wave velocity might help to differentiate dissolution from saturation effects. Again, the pre-injection, water-saturated rock is indicated by point A. An important prediction of Gassmann’s theory (Berryman, 1999) is that the shear modulus of rocks should be independent of fluid saturation. With Gassmann’s theory,  $V_S$  can change only due to change in bulk density. As shown in the figure, increasing  $CO_2$  saturation causes an *increase* in  $V_S$ , due to the *decrease* in rock bulk density. The increase in  $V_S$  is independent of whether saturation is uniform or patchy, and therefore the red and blue curves (points B, C) coincide. In contrast, dissolution, without a change in gas-phase saturation, is indicated by the green arrow. A 3% increase of porosity is indicated by point D, and a 5% increase of porosity is indicated by point D’. Hence, with  $CO_2$  injection, a Gassmann-consistent

saturation effect would cause an *increase* in  $V_S$ , while a chemical dissolution effect would cause a *decrease* in  $V_S$ . Figure 1 also reports the velocity change for scenarios lying between the three end-members. The dashed black line in the figure illustrates the change in  $V_S$  in host rock if dissolution (simulated as a change in the frame properties due to porosity increase) and  $\text{CO}_2$  consumption (simulated as a decrease of  $\text{CO}_2$  saturation) are taken into account. Although S-wave velocities are rarely reported in the literature for injection-monitoring sites, a few field studies (Daley et al., 2006; Wang et al., 1998) and laboratory studies (Wang et al., 1998) reported a non-negligible *decrease* of S-wave velocity upon  $\text{CO}_2$  injections in addition to the expected change in P-wave velocity. Daley et al. (2006) report that P- and S-wave velocities change by  $\sim 500$  m/s and  $\sim 200$  m/s, respectively while injecting  $\text{CO}_2$  in the brine aquifer of the Frio Formation, Texas.  $\text{CO}_2$  storage in deep formations generally takes place at depths below 800 m (Rubin et al., 2004), where temperature and pressure conditions are likely to keep  $\text{CO}_2$  in a liquid state. Under these conditions, the bulk modulus of  $\text{CO}_2$  is 88% smaller than that of water. However, the two fluids have similar densities, with that of  $\text{CO}_2$  slightly lower than water. *Therefore, the observed decrease in S-wave velocity following  $\text{CO}_2$  injection cannot be attributed to a Gassmann-consistent density effect, but is more consistent with a chemical reaction of  $\text{CO}_2$  with the rock frame.*

Differences between the dynamic elastic shear moduli of fluid-saturated rocks measured in the laboratory and those predicted using Gassmann's equations have been reported in the literature both for shaley sandstones (Khazanehdari and Sothcott, 2003; Vanorio, 2007) and carbonate rocks (Vanorio et al., 2008; Adam et al., 2007; Baechle et al., 2005; Rossebø et al., 2005; Assefa et al., 2003; Eberli et al., 2003; Japsen et al., 2002). In these rocks, shear elastic moduli are observed to soften, which the authors attribute to several factors such as rock fabric, clay content, and rock-fluid coupling (*i.e.* fluid viscosity, reactivity, and nature of chemical bonds). Figure 2a plots the change in shear moduli versus the difference between the experimentally fluid-saturated and Gassmann fluid-substituted bulk moduli. Data refer to carbonates saturated with degassed, distilled water (blue diamonds),  $\text{CaCO}_3$  aqueous solution (gray diamonds), and carbonated water (red diamonds). Velocity dispersion caused by high-frequency fluid effects (Mavko and Nur, 1979; Mavko and Jizba, 1991; Gist, 1994; King and Marsden, 2002) impose that differences between the experimentally fluid-saturated and Gassmann fluid-substituted bulk moduli fall within the 1<sup>st</sup> quadrant, meaning that Gassmann's velocity predictions should be lower than ultrasonic, saturated measurements. However, Figure 2a shows that the values of the difference between moduli do not always fall within the 1<sup>st</sup> quadrant, and are sometimes negative ( $V_{\text{meas}} < V_{\text{Gass}}$ ).

These observations imply that there are mechanisms of fluid saturation which oppose those causing high-frequency dispersion. These conditions seem enhanced when the pore fluid is more reactive, which eventually leads the differences between moduli to rotate counterclockwise toward the 3<sup>rd</sup> quadrant (*e.g.* carbonated water, red diamonds). Since the effects of high frequencies on the elastic moduli (and by proxy on velocity) would compete with effects of chemical processes, we hypothesize that the chemical effects on velocity may be more significant under low-frequency (*i.e.* seismic) conditions. This would lead the predictions of Gassmann's theory to either underestimate saturations or overestimate pore pressure in order to match the chemically softened velocities. Adam et al. (2007) showed that in brine-saturated carbonates, the Gassmann-calculated moduli more closely match the moduli measured at high frequencies than those measured at seismic frequencies, reporting this surprising result as a paradox of Gassmann's theory. Figure 2b shows the variation of P- and S- wave velocity upon

several injection cycles of carbonated water in a carbonate rock. Confining and pore fluid pressure were kept constant during each injection cycle. Solid symbols denote velocities measured under full saturation, whereas open symbols denote the dry conditions after each injection cycle. Figure 2b shows that both P- and S- dry velocities decrease with more injection cycles, suggesting a change in the rock frame that might be due to porosity enhancement, changes in stiffness at the grain contacts, or the formation of new, softer mineral phases. In any case, the predicted Gassmann's  $V_P$  (cyan line) based on constant properties of the frame overestimates the ultrasonic velocity.

All these physicochemical phenomena suggest that seismic fluid substitution, under conditions of a complex rock-fluid coupling, is likely to be more than a purely mechanical problem. Chemical effects such as mineralogical changes, dissolution, and precipitation induce changes in the properties of the rock frame (e.g. porosity, stiffness of the grain contacts, permeability), which in turn alter the baseline of Gassmann's equations. *Since Gassmann's equations cannot account for velocity decreases due to changes in the properties of the rock frame, these changes will be necessarily compensated with erroneous estimates of saturation and pore pressure.* The right-hand panel in Figure 2b shows that to accurately assess saturated velocities in these reactive situations, we need relationships describing how velocity varies in chemically-softened rock frames, so that we can adjust the elastic properties of the pre-injected frames (Figure 2 (right)- cyan diamonds).

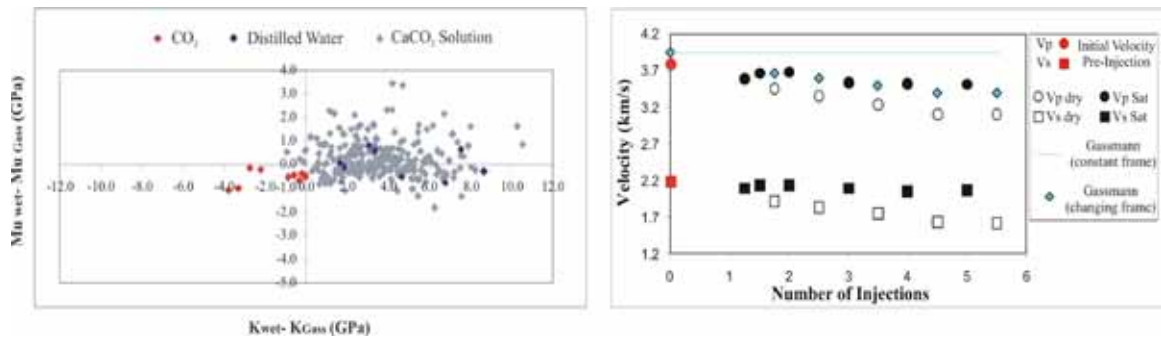


Figure 2. (left) Change in shear moduli versus the difference between fluid-saturated and fluid-substituted bulk moduli. Data refer to core plugs saturated with degassed, distilled water (blue diamonds), CaCO<sub>3</sub> aqueous solution (gray diamonds), and carbonated water (red diamonds) (from Vanorio et al., 2008); (right) variation of dry (open symbols) and saturated (filled symbols) P- and S- wave velocity upon injection of carbonated water (pH=3.8) (data are from Vialle et al., 2009).

We are still far from success in modeling such observations, because we have limited knowledge of how factors such as intrinsic rock properties (e.g. mineral composition, grain size, and permeability), physical conditions (e.g. temperature and pressure), and fluid properties control physicochemically induced changes of observed reservoir rock velocities. This study will show the preliminary results of an integrated approach combining macro-scale measurements, high-resolution pore-scale imaging techniques, and theoretical modeling.