



Contents lists available at ScienceDirect

## Journal of Applied Geophysics

journal homepage: [www.elsevier.com/locate/jappgeo](http://www.elsevier.com/locate/jappgeo)

# AVA seismic reflectivity analysis in carbon dioxide accumulations: Sensitivity to CO<sub>2</sub> phase and saturation

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## ARTICLE INFO

### Article history:

Received 30 September 2009

Accepted 24 November 2010

Available online 2 December 2010

### Keywords:

CO<sub>2</sub> sequestration  
Seismic monitoring  
AVO  
Solubility  
Partial saturation

## ABSTRACT

Seismic monitoring of sequestered carbon dioxide (CO<sub>2</sub>) in underground deposits is a matter of growing importance. The subsurface monitoring of this greenhouse gas is possible due to the marked contrast between the physical properties of natural reservoir fluids and those of carbon dioxide after the injection. This technique makes necessary the investigation of appropriate seismic indicators to link seismic attributes to petrophysical properties, composition and state of the rock as well as pore-fluid type and *in-situ* physical conditions. With this motivation in mind, we use a Biot–Gassmann formulation to model the theoretical P-wave amplitude reflection coefficients vs. angle of incidence in the seismic range when a planar P-wave strikes the interface between a caprock and a porous sandstone which has its pore space saturated by a mixture of CO<sub>2</sub> with brine or oil at different states (supercritical, liquid and gas). The effects of dissolution of CO<sub>2</sub> in oil and the existence of a saturation threshold, above which a free CO<sub>2</sub> phase develops, are included in the computations. Attention is particularly focused on the sensitivity of the classic best-fit amplitude variations with angle coefficients, to different degrees of CO<sub>2</sub> saturation. We conclude from this analysis that the changes in seismic AVA attributes between 30 and 40 degrees can be useful to infer bounds on the CO<sub>2</sub> saturation degree, to detect the presence of immiscible CO<sub>2</sub> phase and, in some cases, to infer the physical state of the accumulations.

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## 1. Introduction

Carbon dioxide is released into our atmosphere during hydrocarbon production and mainly when carbon-containing fossil fuels such as oil, natural gas, and coal are burned during combustion. As a result of the world-wide consumption of such fossil fuels, the amount of CO<sub>2</sub> in the atmosphere has largely increased over the past century. It is now widely accepted that the continued increase in CO<sub>2</sub> concentration is a major agent in global climate change (Metz et al., 2005).

Many carbon dioxide capture and storage projects are being developed worldwide to reduce the emission of greenhouse gases in the atmosphere as a way to mitigate climate changes in a transition period towards the use of more sustainable energies, in accordance with the objectives of Kyoto agreement. The sequestration and geological storage of CO<sub>2</sub> in many cases is a feasible option to accomplish this goal, giving rise to the science of CO<sub>2</sub> sequestration, a new challenge for governments, scientists and engineers (Raistrick, 2008). However this practice requires a careful surveillance to prevent this greenhouse gas from seeping back to the atmosphere or into fresh water aquifers.

In most cases, the appreciable contrast between the physical properties of natural reservoir fluids and those of carbon dioxide allows the utilization of 4D seismic methods as a monitoring tool of the spatial and temporal evolution of this substance after the injection. Very good illustrations of this technique are described by Arts et al. (2004), Chadwick et al. (2005) and Arts et al. (2007) at Sleipner injection field (North Sea, Norway), among other works. In addition, identification of supercritical CO<sub>2</sub> in 3D seismic surveys has been reported (Purcell et al., 2010). While it is accepted that 4D seismic methods are able to monitor the presence or absence of CO<sub>2</sub>, their ability to quantify the saturation and state of this fluid within the reservoir is still under discussion. This makes it necessary to search for reliable seismic indicators for CO<sub>2</sub> saturated geological formations.

It is widely recognized that the dependence of seismic reflection amplitude vs. offset from source to receiver (AVO) or equivalently, amplitude variations with ray angle (AVA) are important tools for reservoir lithology and fluid characterization (Avseth et al., 2005; Castagna and Backus, 1993). With this idea, Brown et al. (2007) suggested an AVO based method to monitor both presence and degree of CO<sub>2</sub> saturation. They showed that variations in the best-fitting AVO parameters before and after CO<sub>2</sub> injection may be seismically noticeable. More recently, Hardage and Silva (2009) presented an AVO model in brine reservoirs oriented to the identification of CO<sub>2</sub>-brine interfaces. However, none of these authors take into account the high variability of the many parameters and state variables involved

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in CO<sub>2</sub> sequestration problems. This led us to model the seismic P-wave reflection coefficient at the top of a layer containing mixtures of CO<sub>2</sub> and brine or oil, for variable saturation and different *in-situ* pore pressure and temperature conditions (e.g. in cold and warm basins). Moreover, taking into account that in oil reservoirs an important fraction of the CO<sub>2</sub> injected can be absorbed (which is the base of *solubility trapping* strategies), following the ideas presented by Carcione et al. (2006), we included these solubility effects in our computations. These results then allowed us to perform a parametric analysis on the corresponding AVO parameters.

From these experiments we conclude that the AVA intercept parameter shows a monotonic decreasing behavior, with very strong variations with respect to the pre-injection state and for low CO<sub>2</sub> saturation, showing slower changes at higher saturation. The gradient AVA parameter also decays substantially in the low CO<sub>2</sub> saturation range, being less sensitive than the intercept. The third AVO parameter (the curvature), related to the far offset information, is the less sensitive of the three, showing changes that in some cases may be well below the seismic resolution. With regards to the dissolution of CO<sub>2</sub> in oil reservoirs, our model estimates allow us to conclude that it would be possible to use time lapse seismic data to detect and monitor the free CO<sub>2</sub> phase, which forms after the oil is completely saturated.

These results suggest that, under certain conditions, seismic AVA parameters can be used not only to establish bounds on CO<sub>2</sub> saturation levels but also to characterize the physical state of this substance in subsurface accumulations and leakages at different depth levels.

## 2. Modeling procedure and main assumptions

The formulation and solution of the energy and amplitude splitting problem when a monochromatic plane compressional wave strikes obliquely at a plane interface between two isotropic porous saturated homogeneous half spaces was treated by different authors, such as Deresiewicz and Rice (1960), Dutta and Odé (1983), Santos et al. (1992) and Ravazzoli (2001). Following the ideas in those papers, in this work the mechanical behavior of the porous media is described in terms of the classic constitutive relations and equations of motion given by Biot (1956, 1962). At the interface, for both reflected and transmitted phases, two reflected compressional waves (fast and slow) and a shear wave are generated. However, it must be remarked that when a low frequency seismic wave propagates through a porous saturated medium, due to fluid viscosity both constituents (solid and fluid) move in phase, and consequently, the model response is equivalent to that resulting from the formulation given by Gassmann (1951). In this connection, since in this work we are interested in frequencies within the seismic range, we do not study slow wave conversions and focus in the fast P-wave reflection coefficient. Nevertheless, and only for selected cases, we also analyze the shear wave reflection coefficient.

In this work, it is assumed that the mixture of CO<sub>2</sub> and brine or CO<sub>2</sub> and reservoir oil at the pore scale can be treated as a viscous single phase effective fluid, as explained in the next section. The dissolution of a fraction of CO<sub>2</sub> and the presence of a remaining free part is taken into account in these computations, whose effect is particularly important for the case of CO<sub>2</sub> injected in oil reservoirs.

We also consider that the CO<sub>2</sub> is uniformly distributed within the pore space in one of the half spaces, forming a layer of thickness larger than the wavelengths of the incident waves. The computation of seismic reflection coefficients for the case of thin layers or spatially variable CO<sub>2</sub> distribution (such as patchy saturation) would require a more complex treatment.

In general, the presence of intrinsic dissipation in wave propagation models lead to a complex frequency dependent reflection coefficient, which produces changes in amplitude and phase of the

reflected waves (Ravazzoli, 2001). Given that for the applications we are only considering viscous friction effects associated to Biot's global flow in homogeneously saturated porous media, which are negligible at low frequencies, the imaginary parts of the reflection coefficients are several orders of magnitude lower than the real parts. Consequently, in the numerical examples we only show their real part, hereafter denoted by  $R_{pp}$  for the P-wave and  $R_{ps}$  for converted shear waves.

To complete the model description, it is important to remark the assumption of no chemical interactions between the pore fluids and the frame, which allows us to employ a fluid substitution procedure to consider that the pore space is saturated by brine or oil and CO<sub>2</sub> in variable proportions. Variations of rock matrix elastic properties with effective pressure (related to the difference between confining and pore pressure), are not taken into account either. However, knowing the experimental effective pressure laws for the rocks under consideration would allow us to incorporate this effect in the computations (Ravazzoli, 2001).

## 3. Physical properties of CO<sub>2</sub> and reservoir fluids

We study the injection of a volume of carbon dioxide  $V_{CO_2}$  in a geologic reservoir in which the pore volume  $V_p$  at the pre-injection state is fully saturated by liquid reservoir fluids such as brine or oil, occupying a volume  $V_l$ . Then, we introduce the total *initial* CO<sub>2</sub> saturation  $S_{CO_2}$  and the liquid saturation  $S_l$  (corresponding to brine or oil), which satisfy the following relations:

$$S_{CO_2} = \frac{V_{CO_2}}{V_p}, \quad S_l = \frac{V_l}{V_p}, \quad \text{with } S_l + S_{CO_2} = 1. \quad (1)$$

According to Batzle and Wang (1992) and Carcione et al. (2006), part of  $V_{CO_2}$  is dissolved into the reservoir fluids and the remaining CO<sub>2</sub> takes the form of a free immiscible phase, giving rise to a two-phase fluid saturation. For simplicity, we leave out capillary pressure effects.

Since dissolution effects are negligible in brine (Batzle and Wang, 1992; Carcione et al., 2006), we only take this effect into account when the reservoir fluid is oil. In this case it is assumed that the CO<sub>2</sub>-saturated oil behaves as a live oil whose physical properties can be obtained using Batzle and Wang (1992) empirical laws. With this idea and following the procedure presented by Carcione et al. (2006), we assume that the amount of CO<sub>2</sub> absorbed in an oil volume can be quantified using the gas-oil-ratio coefficient  $R_G$  in the form given by Batzle and Wang (1992), which represents the maximum volume ratio of liberated gas to remaining oil. Given that  $R_G$  corresponds to standard temperature and pressure conditions, an equivalent ratio  $R'_G$  at *in-situ* conditions is calculated through a mass balance.  $R'_G$  defines a critical saturation threshold  $S_c$  such that for  $S_{CO_2} < S_c$  all CO<sub>2</sub> goes into solution in oil and there is no free CO<sub>2</sub> phase. For  $S_{CO_2} \geq S_c$  the oil absorbs the maximum possible CO<sub>2</sub> and the rest gives rise to a free-CO<sub>2</sub> immiscible phase, with saturation denoted by  $S_{CO_2}^f$ . In this way, we can define the free CO<sub>2</sub> saturation  $S_g$  in the general form:

$$S_g = \begin{cases} 0 & \text{if } S_{CO_2} < S_c \\ S_{CO_2}^f & \text{if } S_{CO_2} \geq S_c, \end{cases} \quad (2)$$

being  $S_l = 1 - S_g$  the liquid saturation. The *effective* physical properties of the oil-CO<sub>2</sub> mixture are then obtained by means of the following rules:

$$\text{mass density } \rho_f^* = S_l \rho_l + S_g \rho_{CO_2} \quad (\text{weighted average}), \quad (3)$$

$$\text{bulk modulus } \frac{1}{K_f^*} = \frac{S_l}{K_l} + \frac{S_g}{K_{CO_2}} \quad (\text{isostress Reuss average}), \quad (4)$$

$$\text{viscosity } \eta^* \approx \eta_{CO_2} \left( \frac{\eta_l}{\eta_{CO_2}} \right)^{S_l} \quad (\text{Teja and Rice, 1981}), \quad (5)$$

where  $\rho_l$ ,  $\rho_{CO_2}$  are the individual liquid and CO<sub>2</sub> densities,  $\eta_l$ ,  $\eta_{CO_2}$  their viscosities and  $K_l$ ,  $K_{CO_2}$  the corresponding bulk moduli. Similar equations to (3), (4) and (5) hold for the CO<sub>2</sub>-brine mixture using (1) with  $S_g \equiv S_{CO_2}$ .

The density, bulk modulus and viscosity of brine and live oil for the given *in-situ* temperature and pressure conditions are computed using the empirical relations given by [Batzle and Wang \(1992\)](#). For the computations we consider a typical brine salinity of 50,000 ppm. and a light oil with reference density equal to 0.78 gr/cm<sup>3</sup>, equivalent to an API gravity equal to 50.

The corresponding properties of CO<sub>2</sub> (density and bulk modulus) for variable temperature and pressure can be computed using some of the general equations of state (EOS) developed for real gases such as [van der Waals \(1873\)](#) or [Peng and Robinson \(1976\)](#) ([McCain, 1990](#)), or some more specific such as [Span and Wagner \(1996\)](#) or [Duan et al. \(1992\)](#). Some of these EOS are implemented as on-line resources.<sup>1</sup>

To our knowledge, there is not a full agreement yet in geophysical literature about which EOS is the most appropriate to represent CO<sub>2</sub> properties at the temperatures and pressures found in geologic reservoirs. Then for our computations, we employ the fifteen-parameter EOS given by [Duan et al. \(1992\)](#), valid for pressures in the range 0–800 MPa and temperatures from 0 to 1000 °C, which guarantees a suitable representation of CO<sub>2</sub> properties at different states. In some cases, for comparison we also used the well known [van der Waals \(1873\)](#) cubic EOS.

To estimate CO<sub>2</sub> viscosity we used the formulas derived by [Fenghour et al. \(1998\)](#) from laboratory experiments, who found that CO<sub>2</sub> viscosity depends on both temperature and pressure. However it must be emphasized that for frequencies in the seismic range the influence of the effective viscosity in seismic velocities and reflection coefficients is minor.

Depending on the *in-situ* pressure and temperature conditions, CO<sub>2</sub> can exist in the subsurface in different phases (gas, liquid, supercritical and solid). We recall that the *critical point* for CO<sub>2</sub> occurs at a temperature  $T_c = 31.1$  °C and a pressure  $P_c = 7.39$  MPa. At temperatures higher than  $T_c$  and pressures higher than  $P_c$ , CO<sub>2</sub> is in a supercritical state, where it is compressible like a gas but with the density of a liquid. This important characteristic of CO<sub>2</sub> behavior is particularly relevant for its underground storage since supercritical CO<sub>2</sub> can fill the available pore volume with minimum buoyancy effects ([Bachu, 2003](#)). Temperatures and pressures near the critical point commonly occur in applications involving CO<sub>2</sub>, such as enhanced oil recovery techniques and sequestration projects ([Meadows, 2008](#)). However, as pointed out by [Bachu \(2003\)](#), the depth at which CO<sub>2</sub> supercritical conditions are met is highly variable and strongly dependent on surface temperature and geothermal gradients, even within a single basin. In addition, the pressure regime of the basin (normal or abnormal), is also very important and is related to its geologic history, existence of sealing faults, permeability barriers and the occurrence of overpressure generation mechanisms ([Osborne and Swarbrick, 1997](#)).

#### 4. Amplitude vs. angle analysis

Variations in the reflection coefficients with angle of incidence are commonly used in reservoir geophysics to infer properties about the lithology and fluid type of reservoir rocks ([Avseth et al., 2005](#); [Mavko](#)

[et al., 1998](#)). In this article, we investigate whether AVA coefficients can be usefully applied to the characterization of CO<sub>2</sub> accumulations, a problem of particular relevance for monitoring its migrations across permeable layers.

For the applications, we consider a 50 Hz plane P-wave striking the horizontal interface between a porous poorly consolidated sandstone, with high porosity and permeability, i.e. with good storage capacity, overlain by a shale layer acting as sealing rock. For the sandstone we consider the following parameters, taken from [Dutta and Odé \(1983\)](#): porosity 30%, permeability 1 Darcy, solid grain bulk modulus 35 GPa, frame bulk and shear moduli 1.7 GPa and 1.855 GPa and grain density 2.65 gr/cm<sup>3</sup>. The corresponding properties of the upper shale layer are: porosity 25%, permeability 0.001 Darcy, solid grain bulk modulus 20 GPa, frame bulk and shear moduli 3.11 GPa and 1.528 GPa and grain density 2.45 gr/cm<sup>3</sup>. The shale rock is assumed to be fully saturated with brine and the sandstone is assumed to be saturated by mixtures of brine and CO<sub>2</sub>, in one case, and miscible mixtures of oil and CO<sub>2</sub> in another case, in variable volumetric proportions. The physical parameters of the fluids at the different physical states are shown in [Table 1](#).

In the near offset domain or below the critical angle, we assumed that the  $R_{pp}$  reflection coefficient as a function of the incidence angle  $\theta$  can be approximated in the usual form:

$$R_{pp}(\theta) \approx A + B \sin^2 \theta + C (\tan^2 \theta - \sin^2 \theta), \quad (6)$$

where the coefficient  $A$  is the so called *intercept*,  $B$  the *gradient* ([Castagna et al., 1998](#)) and  $C$  the *curvature* ([Barnola and White, 2001](#)). The intercept is equal to the normal incidence reflection coefficient and is controlled by the contrast in acoustic impedance between both media. The gradient is more complex in terms of rock properties and is related to contrasts in density, in compressional and shear wave velocities ([Avseth et al., 2005](#)). The third parameter is important at far offsets and near critical angles ([Mavko et al., 1998](#)). Eq. (6) can be used to carry out a parametric analysis on the  $A$ ,  $B$  and  $C$  coefficients to study their sensitivity at different saturation levels by implementing a standard fitting procedure on the results obtained for  $R_{pp}(\theta)$ .

With the aim of analyzing the behavior of the seismic reflectivity at different scenarios, in the following subsections we perform numerical experiments for variable CO<sub>2</sub> saturation, ranging from 0 to 100%, and different physical states (supercritical, gaseous and liquid), according to the location of the temperature and pressure pairs in the CO<sub>2</sub> phase diagram. A linear relationship between *in-situ* temperature and pressure can be obtained by assuming that the pore pressure at any depth  $z$  is hydrostatic, i.e.  $P = \rho_w g z$ , where  $\rho_w$  is formation water density and  $g$  the gravity constant. Also, considering a surface temperature  $T_0$  and a geothermal gradient  $G$ , so that  $T = T_0 + Gz$ , it is straightforward that

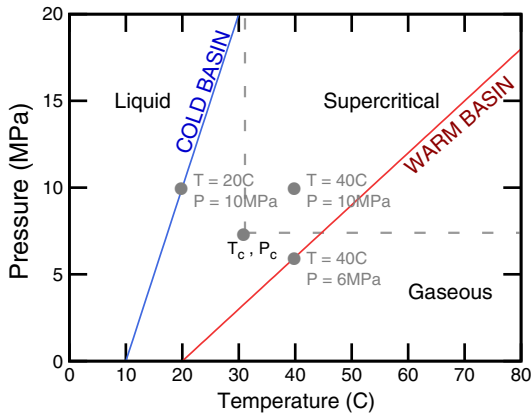
$$P = \left( \frac{\rho_w g}{G} \right) (T - T_0). \quad (7)$$

**Table 1**

Physical properties of brine, oil and CO<sub>2</sub> at different physical states, according to [Batzle and Wang \(1992\)](#), [Duan et al. \(1992\)](#) and [Fenghour et al. \(1998\)](#). The live oil parameters correspond to the maximum CO<sub>2</sub> absorbed.

Physical State	CO <sub>2</sub>	Brine	Saturated Live Oil
Gaseous CO <sub>2</sub>	$K = 0.0049$ GPa	$K = 2.5986$ GPa	$K = 0.4978$ GPa
	$T = 40$ °C $\rho = 0.1498$ gr/cm <sup>3</sup>	$\rho = 1.0287$ gr/cm <sup>3</sup>	$\rho = 0.67$ gr/cm <sup>3</sup>
	$P = 6$ MPa $\eta = 0.1787 \cdot 10^{-3}$ Poise	$\eta = 0.785 \cdot 10^{-2}$ Poise	$\eta = 0.0197$ Poise
Supercritical CO <sub>2</sub>	$K = 0.01397$ GPa	$K = 2.6234$ GPa	$K = 0.2975$ GPa
	$T = 40$ °C $\rho = 0.6452$ gr/cm <sup>3</sup>	$\rho = 1.0304$ gr/cm <sup>3</sup>	$\rho = 0.60$ gr/cm <sup>3</sup>
	$P = 10$ MPa $\eta = 0.4963 \cdot 10^{-3}$ Poise	$\eta = 0.7849 \cdot 10^{-2}$ Poise	$\eta = 0.0197$ Poise
Liquid CO <sub>2</sub>	$K = 0.0931$ GPa	$K = 2.5009$ GPa	$K = 0.3283$ GPa
	$T = 20$ °C $\rho = 0.8535$ gr/cm <sup>3</sup>	$\rho = 1.03607$ gr/cm <sup>3</sup>	$\rho = 0.597$ gr/cm <sup>3</sup>
	$P = 10$ MPa $\eta = 0.8089 \cdot 10^{-3}$ Poise	$\eta = 0.01101$ Poise	$\eta = 0.0496$ Poise

<sup>1</sup> See for example the *Fluid Properties Explorer* of the Consortium for Research in Elastic Wave Exploration Seismology, Calgary University (CREWES) web page: <http://www.crewes.org/ResearchLinks/ExplorerPrograms>. Also The National Institute of Standards and Technology (NIST) *Chemistry WebBook*, <http://webbook.nist.gov/chemistry/>.

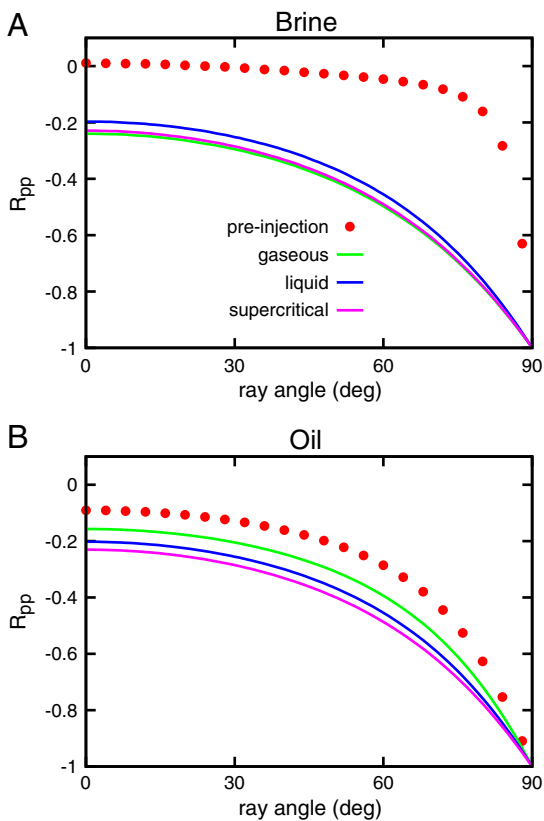


**Fig. 1.** Schematic Temperature vs. Pressure diagram and phase behavior of CO<sub>2</sub> (based on Fig. 3 of Bachu (2003)). The marked points indicate the temperature and pressure values used for the supercritical, gaseous and liquid state of CO<sub>2</sub> in the other figures. In addition, the position of the critical point ( $T_c, P_c$ ) is also indicated.

According to (Bachu, 2003), we can distinguish *warm* basin conditions, where the trajectory in the  $P$  vs.  $T$  diagram is to the right of the critical point and goes through the gas and supercritical regions. The opposite geothermal conditions, defined as *cold*, are those in which the line  $P$  vs.  $T$  is to the left of the critical point (Fig. 1).

4.1. P-wave reflection curves at different physical states

The set of plots in Fig. 2(A)–(B), show the general behavior of  $R_{pp}$  as a function of incidence angle (from 0 to 90°), for the pre-injection case  $S_{CO_2}=0\%$  and for fixed saturation  $S_{CO_2}=50\%$ , for the three CO<sub>2</sub> states previously defined. Fig. 2(A) corresponds to CO<sub>2</sub>-brine and



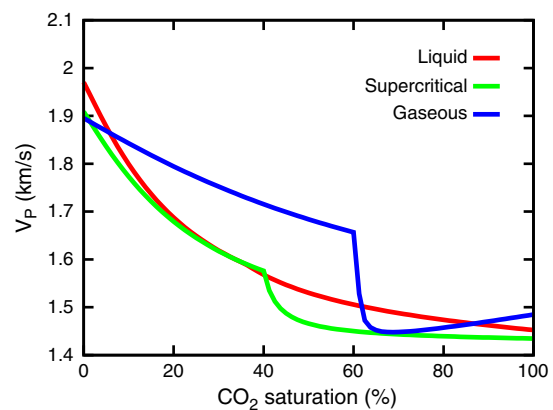
**Fig. 2.** Real part of the P-wave reflection coefficient vs. ray angle for  $S_{CO_2}=50\%$  for (A) brine-CO<sub>2</sub> mixtures and (B) oil-CO<sub>2</sub> mixtures for: gaseous ( $T=40\text{ }^\circ\text{C}$ ,  $P=6\text{ MPa}$ ), supercritical ( $T=40\text{ }^\circ\text{C}$ ,  $P=10\text{ MPa}$ ) and liquid CO<sub>2</sub> ( $T=20\text{ }^\circ\text{C}$ ,  $P=10\text{ MPa}$ ) conditions.

Fig. 2(B) to CO<sub>2</sub>-oil mixture, including dissolution effects in the latter case. Hereafter, according to the scheme in Fig. 1, for the gaseous state we consider a pore pressure  $P=6\text{ MPa}$  and a temperature  $T=40\text{ }^\circ\text{C}$ , a condition that could be found within a warm basin at shallow depths (below 1 km). An intermediate situation, of great practical interest, is that of supercritical CO<sub>2</sub>, which is analyzed by taking  $P=10\text{ MPa}$  and  $T=40\text{ }^\circ\text{C}$ . We also consider the seismic reflectivity in the liquid region, by taking  $P=10\text{ MPa}$  and  $T=20\text{ }^\circ\text{C}$ , a possible case in a cold basin at about 1 km depth. The pre-injection curve shown in Fig. 2 (A)–(B) corresponds to supercritical conditions. The pre-injection curves for gaseous and liquid states are very similar and are not shown for this reason.

The set of curves in Fig. 2 show an AVA class III behavior, according to the standard AVA classification (Castagna et al., 1998). In particular, the plots corresponding to brine at supercritical state are similar to those recently published by Ghaderi and Landro (2009) for Utsira sandstone. As expected, due to the smaller impedance of the lower medium, we obtain a reflection coefficient with a negative real part for normal incidence, becoming more negative for higher angles. However, as will be evident later, for saturations lower than 5% a different AVA class can be found.

In the case of CO<sub>2</sub>-brine mixture, the abrupt change in the reflection coefficient from the pre-injection to the post-injection state, is due to the contrast in physical properties and also because in this case, the CO<sub>2</sub> is a free phase (with no solubility effects). In the CO<sub>2</sub>-oil case these variations are different, showing the influence of the dissolved CO<sub>2</sub> and the critical saturation on the acoustic properties of the live oil.

To analyze this effect in more detail, in Fig. 3 we show the behavior of the P-wave phase velocity for the CO<sub>2</sub>-oil mixture vs. CO<sub>2</sub> saturation for the different temperature and pressure states. The corresponding critical saturations and gas-oil-ratios are:  $S_c=61\%$ ,  $R_G=125$  for the gaseous state,  $S_c=40\%$ ,  $R_G=232$  for the supercritical and  $S_c=36\%$ ,  $R_G=254$  for the liquid state. First, note that the differences in the velocities at the pre-injection state ( $S_{CO_2}=0\%$ ) are due to the different temperature and pressure values of the reservoir oil. The sharp decrease in the wave velocity after  $S_c$  is associated to the existence of the free immiscible CO<sub>2</sub> phase, in agreement with the results found by Carcione et al. (2006). This is not observed for the liquid state due to the physical properties of the saturated oil and the high density of the liquid CO<sub>2</sub>. Also, due to the lower absorption of CO<sub>2</sub> in oil at the temperature and pressure conditions for gaseous CO<sub>2</sub>, for this state we observe a velocity higher than the other states. This results in a smaller reflection coefficient (in absolute value) as seen in Fig. 2(B). Moreover, given that  $R_{pp}$  is plotted at  $S_{CO_2}=50\%$ , the curves for the liquid and supercritical states are above the corresponding critical saturation, having a free CO<sub>2</sub> saturation. This results in smaller



**Fig. 3.** P-wave phase velocity vs. saturation for CO<sub>2</sub>-oil mixture at gaseous ( $T=40\text{ }^\circ\text{C}$ ,  $P=6\text{ MPa}$ ), supercritical ( $T=40\text{ }^\circ\text{C}$ ,  $P=10\text{ MPa}$ ) and liquid CO<sub>2</sub> ( $T=20\text{ }^\circ\text{C}$ ,  $P=10\text{ MPa}$ ) conditions.

velocities and higher reflection coefficients than for the gaseous state, in which the critical saturation is above  $S_{CO_2} = 50\%$  and consequently, there is no free  $CO_2$  phase for this particular experiment.

We conclude that, despite of the complex behavior due to the dissolution effects, which reduce the contrast in seismic reflectivity between pre-injection to post-injection states (compared to the  $CO_2$ -brine case), we observe that the discrimination of the *in-situ*  $CO_2$  physical state may be more feasible in oil than in brine injection sites. The sensitivity of the P-wave reflection coefficient to  $CO_2$  saturation will be studied in detail in Subsection 4.3 by analyzing the behavior of the corresponding AVA coefficients.

#### 4.2. Influence of temperature and pressure

Considering the uncertainties in the *in-situ* formation, temperature and pore pressure, and to assess their influence on the seismic reflectivity, in Figs. 4 and 5 we plot the variations of  $R_{pp}$  with those state variables, assuming that they vary independently. We restricted to  $\theta = 30^\circ$  and a limited number of  $CO_2$  saturations steps (0%, 10%, 20%, 60% and 100%).

In Fig. 4 we show the model computations for a fixed supercritical pressure  $P = 10$  MPa, and temperatures ranging from 10 to 50 °C. In Fig. 4(A) we can see that for  $CO_2$ -brine fluids and for temperatures lower than 45 °C the reflection coefficient becomes more negative with increasing temperature. The most pronounced changes are observed for the minimum saturations.

In the case of  $CO_2$ -oil mixture, shown in Fig. 4(B),  $R_{pp}$  shows low sensitivity to temperature variations, except for high saturations. The jump between the 20% and 60% saturation curves is due to the passage through the critical saturations (for instance, recall that for  $P = 10$  MPa

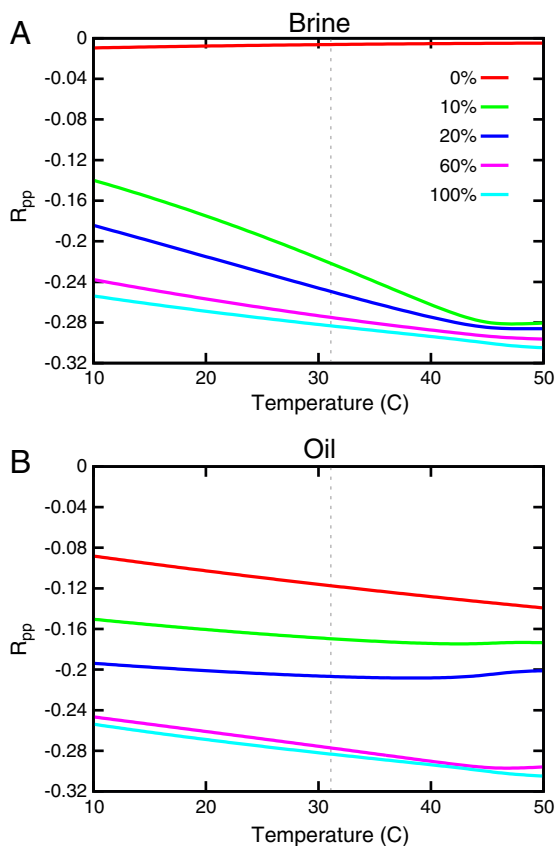


Fig. 4. Real part of the P-wave reflection coefficient vs. formation temperature for fixed pressure  $P = 10$  MPa and angle  $\theta = 30^\circ$ . The dotted vertical line denotes the critical temperature at  $T_c = 31.1$  °C.

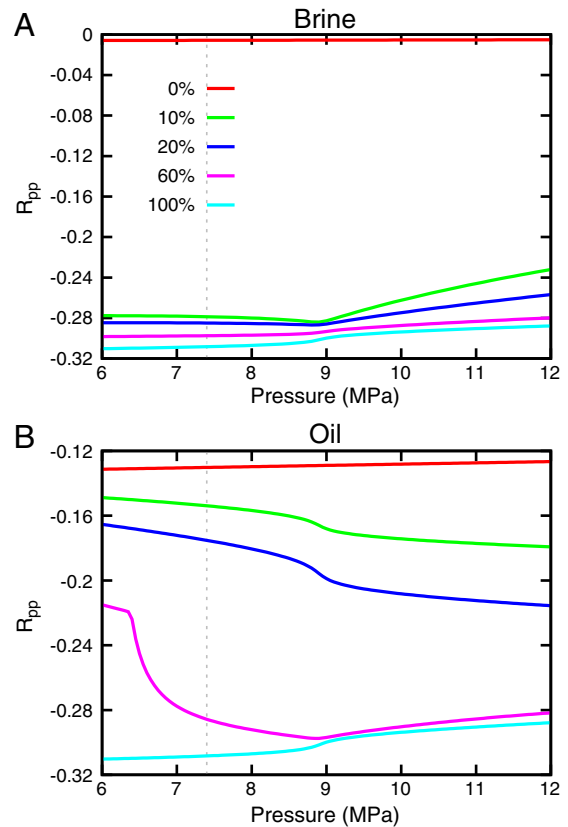


Fig. 5. Real part of the P-wave reflection coefficient vs. pore pressure for fixed temperature  $T = 40$  °C and angle  $\theta = 30^\circ$ . The dotted vertical line denotes the critical pressure at  $P_c = 7.39$  MPa.

and  $T = 40$  °C,  $S_c = 40\%$ ), showing the increase in  $R_{pp}$  due to the presence of the free  $CO_2$  phase.

The curves of  $R_{pp}$  vs. pressure for a supercritical temperature  $T = 40$  °C for  $CO_2$ -brine (Fig. 5(A)), show an almost constant behavior with pressure, with a noticeable change of trend at about 9 MPa, associated to the transition zone from gaseous to supercritical  $CO_2$  for that temperature, an effect that was also corroborated using van der Waals (1873) EOS. Similar results were also found for normal incidence.

The behavior of  $R_{pp}$  vs. pressure in the case of  $CO_2$ -oil mixture, shown in Fig. 5(B), is very different, once again, due to the variable  $CO_2$  dissolution in oil and the effect of the critical saturation. Nevertheless, the slight change in the transition zone from gaseous to supercritical  $CO_2$  can still be observed.

From both Figs. 4 and 5 we observe that as  $CO_2$  saturation increases, the effects of pressure and temperature are less marked. These results also clearly show the necessity of accurate estimations of pressure and temperature for a proper calibration of theoretical models and real time lapse seismic data, particularly at the early stages of injection, in which the errors could be significant.

#### 4.3. AVA coefficients vs. partial $CO_2$ saturation at different conditions

In the next set of Figs. 6, 7 and 8, we plot the coefficients  $A, B, C$  to study their sensitivity at different saturation levels and physical states, by fitting Eq. (6) to the numerical results obtained for  $R_{pp}(\theta)$ .

For the case of  $CO_2$ -brine (dotted lines), we found that the intercept parameter  $A$  (Fig. 6), shows a monotonic decreasing behavior for the three physical states under consideration. These variations are more pronounced for  $CO_2$  in liquid state, with significant percentage changes in the range from 5% to 40%. This is due to the behavior of the compressional velocity, which remains almost constant for  $CO_2$  saturations greater than about 40%. In the

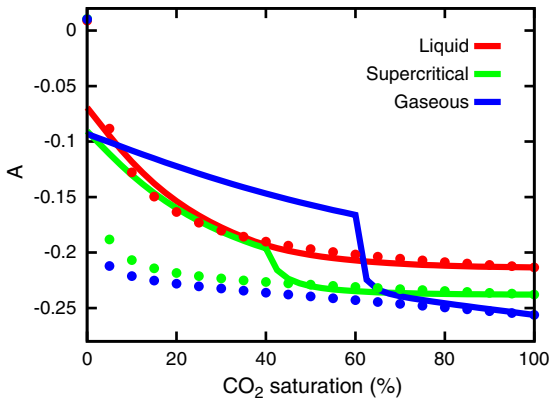


Fig. 6. Intercept (A) parameter vs. CO<sub>2</sub> saturation for brine-CO<sub>2</sub> mixtures (dotted lines) and oil-CO<sub>2</sub> mixtures (solid lines) at the different physical states.

same saturation range the variation of *A* for supercritical and gaseous CO<sub>2</sub> is much lower but still noticeable for the reservoir fluids considered. This allows us to clearly distinguish the liquid state from the gaseous and supercritical states.

The variations of *A* in the CO<sub>2</sub>-oil mixture (solid lines) for saturations below the critical ones are pronounced for all states, being maximum for supercritical and gaseous states. The effects of dissolution of CO<sub>2</sub> in oil are responsible for such strong variations in this coefficient and in this case the gaseous state can be distinguished from the other two.

It is worthwhile to mention that for saturations lower than 5%, the intercept takes slightly negative values, consistent with an AVA Class II case.

Regarding the gradient *B* (Fig. 7) in CO<sub>2</sub>-brine mixtures, it can be seen that it is always negative showing a trend similar to that of the intercept, except for the gaseous CO<sub>2</sub> state, in which a slightly opposite trend is observed. The most significant variations take place for CO<sub>2</sub> in liquid state, which can be useful to distinguish this particular state from the other two, with a gradient almost insensitive to saturation.

In the case of CO<sub>2</sub>-oil saturation, slow and similar variations are observed below the critical saturations, being more pronounced for the liquid and supercritical states.

The curvature coefficient *C* (Fig. 8), compared with the *A* and *B* coefficients, is the least sensitive of the three, both, to the fluid type and saturation level of the injected CO<sub>2</sub> (note that to enhance the behavior of the curves the vertical axis of Fig. 8 is not the same as in Figs. 6 and 7). For both fluid types, we only found significant changes for CO<sub>2</sub> at the liquid state and for saturations in the range from 0 to about 40%. For higher saturations, the correct determination of such small changes may be strongly limited by the seismic resolution. In

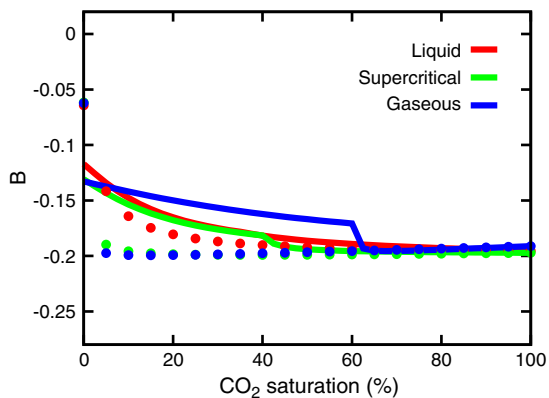


Fig. 7. Gradient (B) parameter vs. CO<sub>2</sub> saturation for brine-CO<sub>2</sub> mixtures (dotted lines) and oil-CO<sub>2</sub> mixtures (solid lines) at the different physical states.

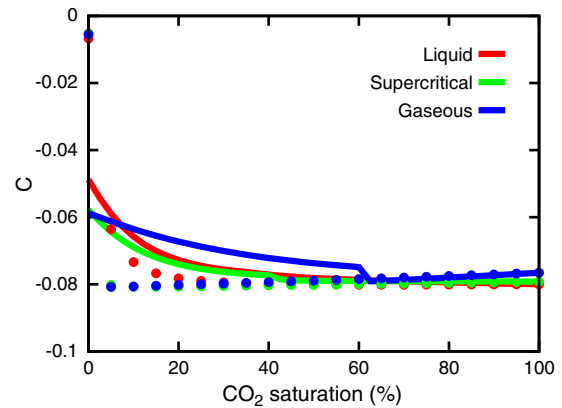


Fig. 8. Curvature (C) parameter vs. CO<sub>2</sub> saturation for brine-CO<sub>2</sub> mixtures (dotted lines) and oil-CO<sub>2</sub> mixtures (solid lines) at different physical states.

this sense, Brown et al. (2007) pointed out that AVA variations on the order of 5% are seismically detectable. Using this numerical threshold, we can state that variations in the parameter *C* do not contain much information with respect to these pore-fluid variations and consequently an AVO analysis based solely on *A* and *B* may be sufficient, being *A* the most sensitive for the determination of the CO<sub>2</sub> saturation state.

#### 4.4. Effect of the EOS

In Fig. 9, we illustrate the coefficients *A* and *B* vs. CO<sub>2</sub> saturation, comparing the results obtained using van der Waals (1873) and Duan

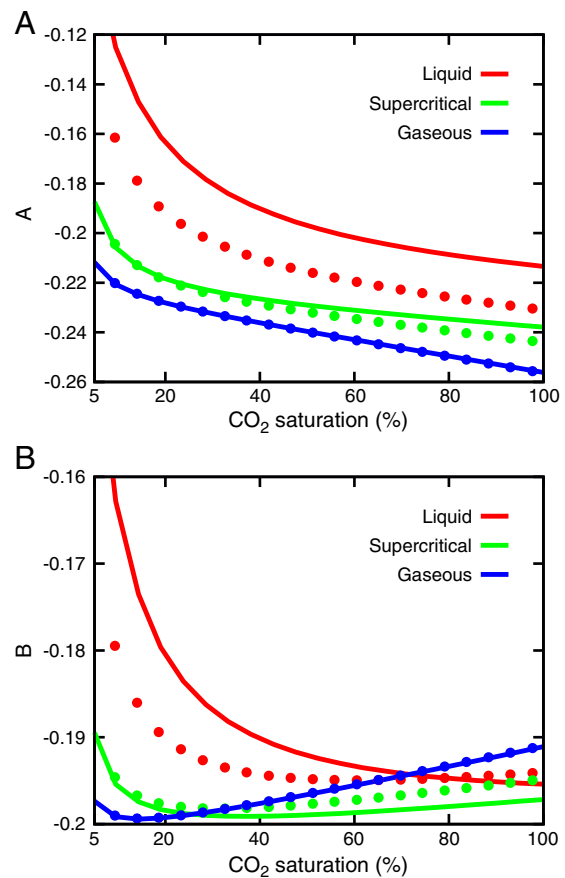
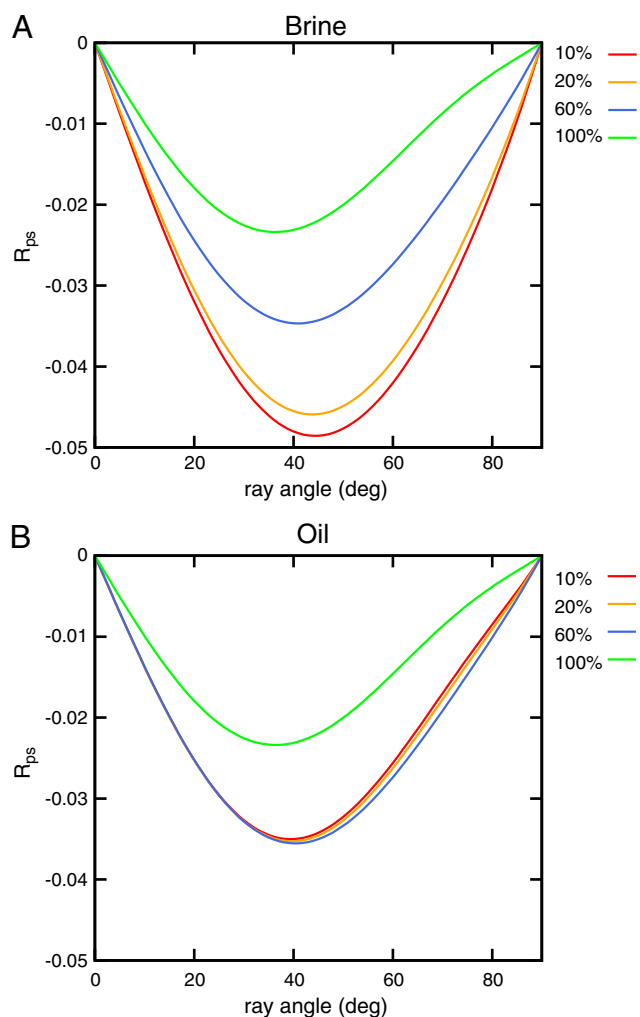


Fig. 9. *A* and *B* vs. CO<sub>2</sub> saturation for brine-CO<sub>2</sub> mixtures using Duan et al. (1992) (solid lines) and van der Waals (1873) (dotted lines) EOS at CO<sub>2</sub> supercritical conditions. To enhance the differences between the curves, saturations lower than 5% are not shown.

et al. (1992) equations of state. We only show the results corresponding to mixtures of CO<sub>2</sub> with brine at the three physical conditions, to observe the behavior of the EOS at the different states. We excluded from this figure CO<sub>2</sub> saturations lower than 5% to enhance the small discrepancies between the curves. From the results, we observe that for the supercritical and gaseous states, both EOS show an excellent agreement. The most important differences are observed for liquid CO<sub>2</sub> conditions, in which *A* and *B* may be underestimated when using van der Waals (1873) EOS. However this only affects the second decimal place. From these experiments we can conclude that, for seismic modeling applications, the choice of an EOS should not be a main concern since it does not change the results significantly.

#### 4.5. Shear wave conversion

To conclude this work, we investigate whether shear wave reflections at the top of the CO<sub>2</sub> accumulation could be used for monitoring purposes. With this motivation, we modeled the shear wave reflection coefficient  $R_{ps}(\theta)$  for mixtures of CO<sub>2</sub> with brine or oil at the different physical conditions under consideration. In Fig. 10(A)–(B) we show  $R_{ps}$  for angles in the range 0–90° for the case of gaseous CO<sub>2</sub> injected in brine and oil, respectively. Although the amount of energy conversion from compressional to shear wave mode is very low, we note that for this particular state  $R_{ps}$  at angles above 30



**Fig. 10.** Shear wave reflection coefficient vs. ray angle (A) for brine-CO<sub>2</sub> mixtures and (B) oil-CO<sub>2</sub> mixtures at gaseous CO<sub>2</sub> conditions ( $T = 40$  °C,  $P = 6$  MPa) for different fixed saturations.

degrees is very sensitive to the CO<sub>2</sub> saturation degree in the case of CO<sub>2</sub>-brine mixtures. This sensitivity is not observed when the reservoir fluid is oil, due to the solubility effects, which reduce the amount of free CO<sub>2</sub>. However it can be useful as a rough indicator of the presence or absence of CO<sub>2</sub> in the reservoir oil.

#### 5. Conclusions

We have analyzed the behavior of the compressional and shear wave reflection coefficients vs. angle of incidence at the top of a plane CO<sub>2</sub> accumulation within a poorly consolidated sandstone and beneath a shale caprock. Considering different temperatures and pore pressures corresponding to gaseous, supercritical and liquid CO<sub>2</sub> states, and using a standard three term  $R_{pp}$  approximation we have also modeled the variations of the AVA parameters *A*, *B*, *C* as a function of partial saturation for CO<sub>2</sub>-brine and CO<sub>2</sub>-oil mixtures.

In the particular case of CO<sub>2</sub> injected in oil reservoirs, the dissolution of variable fractions of CO<sub>2</sub> was taken into account in our model. Except for CO<sub>2</sub> at the liquid state, our model predicts a sharp decrease in the wave velocity for saturations higher than the critical, associated to the presence of a free CO<sub>2</sub> phase. This behavior is also clearly noted in the intercept *A*, being less pronounced in *B* and *C*.

The intercept and gradient parameters generally have a monotonic decreasing behavior, with a strong variation with respect to the pre-injection state. The most important percentage variations are always observed in the intercept, this parameter being the most sensitive to CO<sub>2</sub> saturation. In all cases analyzed, the coefficients *A* and *B* show significant changes for CO<sub>2</sub> saturations under about 40% or lower than the critical threshold. The curvature *C* does not bring much more information about saturation, since in most cases its variations are smaller than those observed in *A* and *B*. The lack of sensitivity of AVA parameters for very high saturations imposes a serious limitation to any attempt to quantify CO<sub>2</sub> saturation degree using AVA information.

In the particular case of oil reservoirs, our model estimates allows us to conclude that it would be possible to use time lapse seismic data to detect and monitor the free CO<sub>2</sub> phase, which forms after the oil is completely saturated. This is of particular interest in sequestration based in solubility trapping.

In some cases, reservoir temperature and pressure uncertainties can lead to significant errors in the modeled reflection coefficients, particularly at low CO<sub>2</sub> saturations. However, variations in AVA coefficients derived from implementing different equations of state for carbon dioxide are not significant.

With regards to the shear wave reflection coefficient at the top of the CO<sub>2</sub> accumulation, we found that the amount of energy conversion from compressional to shear waves is low but particularly sensitive to saturation for gaseous CO<sub>2</sub> injected in brine. Although this sensitivity is not observed when the reservoir fluid is oil, the analysis of shear wave mode conversions can be useful as a rough indicator of the presence or absence of CO<sub>2</sub> in the reservoir oil, which can be useful for monitoring purposes.

We also studied the sensitivity of the AVA coefficients to the thermodynamic conditions of the CO<sub>2</sub> at the subsurface. In the case of CO<sub>2</sub>-brine mixtures it seems possible to discriminate a change in state from supercritical or gaseous to liquid (and vice versa), by analyzing the time lapse changes in *A* and *B*. For CO<sub>2</sub>-oil mixtures this discrimination would be possible by means of the intercept, when the CO<sub>2</sub> changes to gaseous state. This suggests the possibility of using seismic reflection data to characterize the physical state of the CO<sub>2</sub> accumulated into brine or oil reservoirs, even with normal incidence data only. Moreover, the study of changes in AVA parameters over time may help to establish bounds on CO<sub>2</sub> saturation degree particularly at the early stages of accumulation below the caprock, assuming uniformly distributed CO<sub>2</sub>.

The same kind of theoretical analysis can be performed for any other reservoir with a proper calibration of the rock physics model for

the CO<sub>2</sub> sequestration site. This can be useful to assess the applicability of the seismic reflection method for monitoring purposes.

### Acknowledgements

The results presented here have been obtained in the CO2ReMoVe project, which envisages the development of technologies and procedures for monitoring and verifying geological CO<sub>2</sub> storage. The financial support of the European Commission and the industrial consortium involved is greatly appreciated.

Partial financing was also received from CONICET PIP 112-200801-00952 and by Agencia Nacional de Promoción Científica y Tecnológica PICT 03-13376. The authors thank William Harbert and an anonymous reviewer for their critical and accurate reviews of the original manuscript which was greatly improved by their comments. Also, to Dr. J. Germán Rubino for writing the code for CO<sub>2</sub> equations of state.

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