

## Developing the Rock Physics Model – Improved Carbon Dioxide Mixing Rules for Carbon Capture and Storage

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### Introduction

Current energy policies focus on maximising current hydrocarbon resources and minimising carbon emissions. Consequently, fresh importance is placed on understanding the behaviour and properties of CO<sub>2</sub> for the following reasons:

- CO<sub>2</sub> is a natural constituent of hydrocarbon reservoirs. Concentrations vary from 2 - 80% and the presence of CO<sub>2</sub> can greatly influence the hydrocarbon behaviour.
- CO<sub>2</sub> is widely used for Enhanced Oil Recovery (EOR), in both miscible (WAG) and immiscible (cyclic) programmes.
- The geological storage of CO<sub>2</sub> is an effective means of curbing carbon emissions, *Carbon Capture & Storage, CCS*.

To date, the reservoir fluids of principle concern to rock physics community have been hydrocarbon fluids (oils and gasses) and brine. It is now apparent that a better understanding of CO<sub>2</sub> is of paramount importance.

### CO<sub>2</sub> Properties

It is well known that CO<sub>2</sub> is not a simple fluid. Whilst gaseous (~2kg/m<sup>3</sup>) at surface temperatures and pressures, it exhibits supercritical (sc) behaviour beyond 7.4MPa and 31°C (464kg/m<sup>3</sup>) which correspond to approximately 840 m depth at a normal onshore geothermal gradient of 25°C/km. At that geothermal gradient a liquid phase of CO<sub>2</sub> (680-690 kg/m<sup>3</sup>) may precede the supercritical phase transition. In the reservoir column, CO<sub>2</sub> could vary in density by almost three orders of magnitude and be in all four fluid states (vapour, gas, liquid and super critical (scCO<sub>2</sub>)).

In addition to this, CO<sub>2</sub> is a non-polar compound and thus has no intermolecular interactions when pure. However, when mixing with polar molecules such as water/brine a quadrupole is induced on the CO<sub>2</sub> molecule [1]. This will affect the behaviour (viscosity, supercritical point etc) of the CO<sub>2</sub> fluid according to the molecules with which it's interacting.

### CO<sub>2</sub> storage

The reservoirs targeted for CO<sub>2</sub> storage may be residual hydrocarbon fields or saline aquifers. Within one reservoir, CO<sub>2</sub> will be stored in four principal forms (Figure 1). The proportions of these forms will change within time, with a tendency to increased storage security.

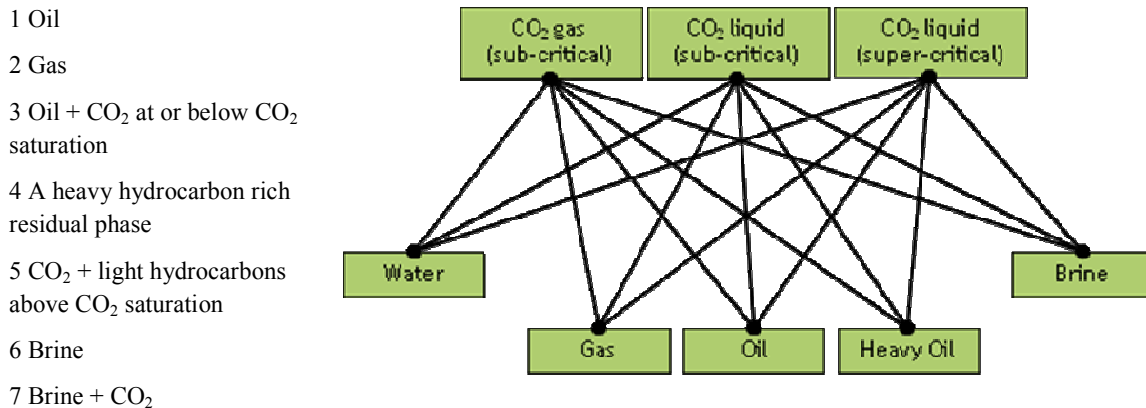


**Figure 1:** Both the proportion of CO<sub>2</sub> & the security of that stored volume increases with time (left to right) from an injected fluid to a mineral precipitate

At typical reservoir depths, CO<sub>2</sub> will be injected in the supercritical state. Thus sequestration scenarios need to model both scCO<sub>2</sub> and the associated property changes when

- CO<sub>2</sub> migrates through the host rock in buoyancy driven plumes.
- CO<sub>2</sub> dissolves into the *in situ* reservoir fluids.
- Dissolved CO<sub>2</sub> sinks in density-driven convection.
- Water/scCO<sub>2</sub> emulsions and dissolved CO<sub>2</sub> react with reservoir cap rock minerals

In geologic formations CO<sub>2</sub> will be interacting with several different fluids in several different phases. Not only will the CO<sub>2</sub> affect the behaviour of the reservoir fluids, the mixing components will influence the behaviour of the CO<sub>2</sub>, shifting the critical point to higher temperature and pressures. Given this, it is possible to have seven fluid phases present within a single field, Figure 2.



**Figure 2:** The seven principal fluid phases likely to be present in a single reservoir, and the multiple mixing scenarios for CO<sub>2</sub> with pure H<sub>2</sub>O, brine & hydrocarbons

### An Equation of State (EoS) for CO<sub>2</sub> and its mixtures:

Conventional fluid properties used in reservoir models rely on mixing models based on cubic equations of state (EoS) for a single fluid, including, although not limited to, Peng-Robinson [2] or Soave-Redlich-Kwong [2]. These models are only valid for pure CO<sub>2</sub>, and their good accuracy (<5%) is restricted to conditions below or away from the critical point. They also produce unsatisfactory predictions for the *deviant behaviour* of CO<sub>2</sub> when mixing with other chemical species.

A well known exception to these mixing models is a CO<sub>2</sub>-specific EoS developed by Span & Wagner [3]. This EoS was developed to predict the behaviour of CO<sub>2</sub> at elevated temperatures and pressures for industrial means, including density and bulk modulus for pure CO<sub>2</sub> at temperatures and pressures past the critical point of 305 K (31.85 °C), 7 MPa, and up to 523 K (249.05 °C) and 30 MPa (~4350 psi) respectively. Although significantly more applicable than the preceding cubic EoS, the accuracy deviates close to the critical point and the model is limited when dealing with the mixtures of fluids likely to be present in a reservoir and the subsequent *deviant properties* of CO<sub>2</sub>.

An alternative to these more traditional cubic EoS is the *Statistical Associating Fluid Theory (SAFT)* developed from statistical mechanics. This is a Helmholtz free energy EoS that predicts the effects of intermolecular interactions on the bulk behaviour of the fluid, from the microscopic to the macroscopic [4]. It has been the most successful EoS to date for predicting phase behaviour close to the critical point and has many industrial applications as a result. Recent research has also focused on predicting the behaviour of water and salt mixtures for geologic purposes [5].

Thermodynamic expressions are mathematically manipulated to find bulk material properties, predict phase equilibria and other chemical properties. Both EOR and geologic sequestration are dynamic systems, and the chemical reaction between the fluid and the reservoir rock, or even within the fluid – e.g. precipitation of asphaltenes, must be accounted for. The flexibility of SAFT, which is unique to the specific attributes of *individual* fluid mixtures, provides a series of mathematical formulae which can address the fluid properties of an interacting CO<sub>2</sub> *mixture* under reservoir conditions

### **Applications**

The development of a SAFT EoS and mixing model for CO<sub>2</sub> within the current rock physics model has potential to greatly enhance the existing geophysical tool box and integrated workflows. The current SAFT module allows the user to predict fluid properties of CO<sub>2</sub> mixing with brines (of variable composition) at a given temperature and pressure. Using updated initial reservoir fluid properties in the rock physics model, gives a means to reliably assess sites and evaluate the dynamic properties of CO<sub>2</sub> (gas, liquid, scCO<sub>2</sub>, aqueous and hydrocarbon solutions) through 2D & 3D time lapse studies. This is particularly important for CCS feasibility and monitoring:

**Feasibility:** The effects of reservoir composition (brine composition, residual hydrocarbons: type and their proportion) upon the injected CO<sub>2</sub> can be modelled, as can the effects of overpressure, temperature of injection, dispersion pathways etc. Understanding the variation in the state of CO<sub>2</sub> across the reservoir is integral to CCS site assessments.

**Monitoring:** Figure 1 illustrates how the principle form of CO<sub>2</sub> will change depending on the time in storage and the mixture in which it exists. As the fluid behaviour varies, significant changes in its acoustical signature may be detectable.

**Example (Figure 3):** We have used the SAFT function to model a scenario where supercritical CO<sub>2</sub> has been injected at depth into brine sand and become structurally trapped (at an undetermined time after injection). Over time a proportion of the injected volume will slowly dissolve into the reservoir fluids, and this CO<sub>2</sub> in solution is also modelled. Note a variation between the seismic response of CO<sub>2</sub> in solution and scCO<sub>2</sub>, Figures 3 a) & b). Figure c) shows a residual plot of scenario b).

### **Summary**

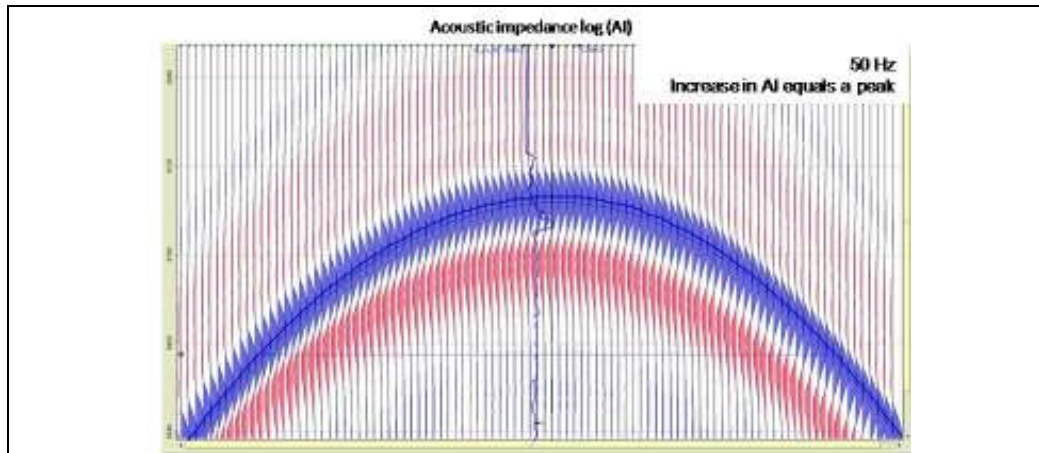
The SAFT EoS is an improved mixing model for CO<sub>2</sub> with water, brine and hydrocarbons. Unlike cubic EoSs, SAFT mixing rules allow accurate CO<sub>2</sub> modelling close to its critical point, and they account for the deviant behaviour caused by additional chemical species present in the reservoir. Thus, the SAFT mixing model offers a method to accurately predict, monitor and verify the properties of CO<sub>2</sub> over the lifetime of a CCS project.

### **Acknowledgements**

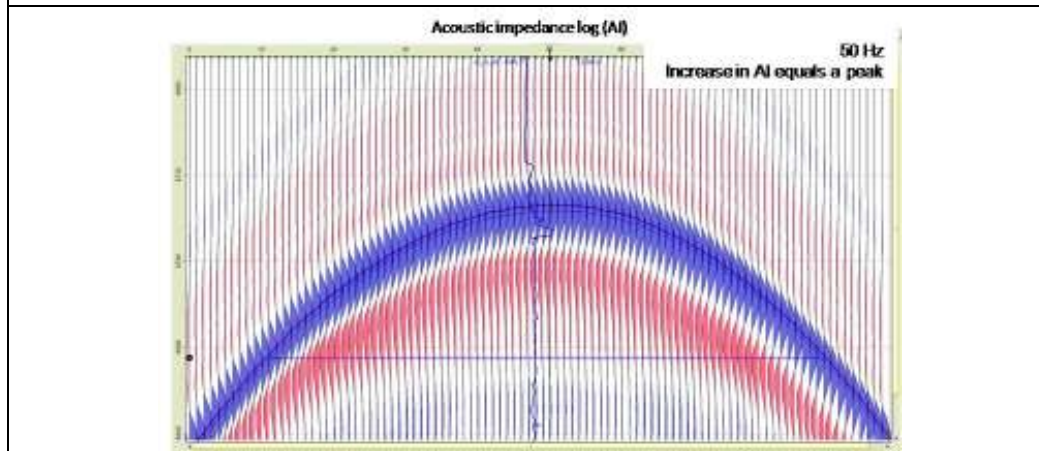
We thank our colleagues at Ikon Science for their support & permission to present this work

### **References**

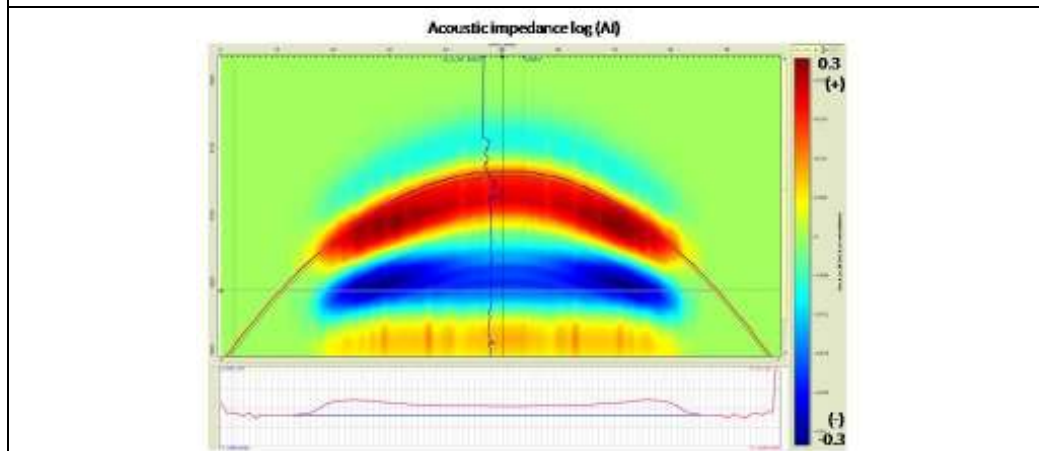
1. Hemptinne, J., Mougine, P., Barreau, A., Ruffine, L., Tamouza, S., and Inchekel, R., 2006. Application to Petroleum Engineering of Statistical Thermodynamics Based Equations of State. *Oil and Gas Science and Technology - Rev IFP* 61(3): 363-386.
2. Sun, L., Zhao, H., Kiselev, S., and McCabe, C., 2005. Predicting mixture phase equilibria and critical behaviour using the SAFT-VRX Approach. *Journal of Physical Chemistry B* 109(18): 9047-9058
3. Span, R., and Wagner, W., 1996. A new equation of state for carbon dioxide covering the fluid region from the triple-point temperature to 1100 K at pressures up to 800 MPa. *Journal of Physical and Chemical Reference Data* 25(6): 1509-1596.
4. Button, J., and Gubbins, K., 1999. SAFT prediction of vapour-liquid equilibria of mixtures containing carbon dioxide and aqueous monoethanolamine or diethanolamine. *Fluid Phase Equilibria*. 158-160:175-181.
5. Ji, X., and Adidharma, H., 2008. Ion-based SAFT-2 to represent aqueous multiple-salt solutions at ambient and elevated temperatures and pressures. *Chemical Engineering Science* 63:131-140.



(a) Simple 2D anticline model containing blocky sands. Overburden consists of shale and brine saturated thin sands. An increase in acoustic impedance between the brine case and sands saturated with CO<sub>2</sub> in solution causes a prominent peak reflection



(b) A fluid contact is added to the blocky sand. A scCO<sub>2</sub> cap is injected above the CO<sub>2</sub> in solution. The greater increase in acoustic impedance, due to the associated increase in Rho & Vp values for scCO<sub>2</sub> causes a brightening of the positive peak. At the contact between scCO<sub>2</sub> and the less dense CO<sub>2</sub> in solution, a weak trough develops.



(c) A residual plot (b-a) reveals the scCO<sub>2</sub> case is ~15% brighter than CO<sub>2</sub> in solution. A small negative residual across the contact results from the difference between a weak positive peak (a) and a weak negative trough (b).

**Figure 3** 2D model demonstrating the changing seismic response observable between scCO<sub>2</sub> and CO<sub>2</sub> in an aqueous solution. Reflectivity traces are 0° incidence