

Influence of cooling and heating rate on CO₂ condensation and evaporation observed in a saturated synthetic rock sample

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Summary

The possibility of reducing carbon dioxide (CO₂) emissions into atmosphere by capture and storage into subsurface reservoirs has led to many different studies related to seismic monitoring of geologically stored carbon to aid in the interpretation of field seismic observations, simultaneous ultrasonic measurements of wave velocities are being conducted on a variety of porous materials. These materials include synthetic sintered alumina, shales, sandstones, and carbonates. The results of such measurements will improve the models obtained from related seismic surveys.

This paper focuses on the effects of CO₂ as a pore fluid on the overall rock seismic response. Laboratory measurements using a fully CO₂ saturated synthetic sample have been conducted over a variety of temperatures and pressures representative of subsurface conditions in which CO₂ can exist in a gas, liquid, or supercritical state. Although full CO₂ saturation is not expected in most *in situ* cases, where pore space will likely be shared with brine or hydrocarbons, this work provides an end member understanding of the evolution of seismic responses resulting from changes in the phase state of CO₂. However, we have observed in these experiments that there is a delay in the temperature at which the gas-to-liquid and liquid-to-gas phase transition occurs during isobaric heating and cooling experiments, which appear controlled, in large part, by the rate of change of temperature and by whether the phase transition is crossed from low to high temperatures or *vice versa*. The time to achieve equilibrium suggested that thermal responses could in part be responsible for the delays. To further investigate this observation a simplified model, the 'lumped capacity model,' was implemented to estimate the time required to reach a desired temperature

Introduction

Seismic velocities within a target formation change in response to the injection of CO₂. These changes reflect the influence of the injected CO₂ fluid on the related elastic moduli of the saturated target rock at various pressures and temperatures. The velocity changes are evident in time-lapse vertical seismic profiles (VSP) as strong reflectors appearing within the injection region (e.g. Zhou et al., 2010). To better understand these changes, investigators measure the elastic properties of the typical target rocks expected in such surveys using a variety of temperatures, heating and cooling rates, confining and pore pressures, and assorted pore fluids. At present, this study builds on previous work done by Yam (2011) and Njiekak et al (2013) where a large quantity of dynamic and static measurements have been recorded using both natural and synthetic samples. In particular, recent modifications to vital pieces of laboratory equipment have allowed for more thorough and efficient measurements of both heating and cooling cycles, in addition extending CO₂ pore fluid pressurization experiments to lower pressures and temperatures. During recent runs, it has become obvious that there are a number of items that workers must be aware of when conducting these types of experiments. The remainder of this abstract will focus primarily on the results of measuring a highly porous high-fired alumina sample saturated with CO₂.

Theory and Method

To investigate the effects of the CO₂ fluid, both strain and ultrasonic measurements have been conducted on the synthetic sample. Strain is measured using a pair of single element 350 Ω gauges. Ultrasonic travel times are measured using 1 MHz compression-wave (P-wave) and shear-wave (S-wave) transducers mounted on aluminum end caps; typically there is one P-wave and one S-wave transducer stacked on each end cap. The sample is a 5.08 cm segment of porous ceramic (high fired alumina) rod. The sample is sealed between the end caps and placed in pressure vessel filled with hydraulic fluid. An ultrasonic pulser/receiver is used to send pulses to the set of transducers on the 'pulser' end cap, and receives the transmitted signal through the transducers on the 'receiver' end cap, under a variety of pressures and temperatures. These end caps are calibrated by performing pressurization/depressurization runs at specified temperatures with no sample placed between them. The recorded travel times are later subtracted from the actual sample data to remove the effects of the end caps. Once assembled and placed in the pressure vessel, the sample is vacuumed for at least 12 hours after which several 'dry' pressurization/depressurization runs are completed at various temperatures. The dry runs are completed to measure the response of the unsaturated rock. Following the dry runs, several similar runs are completed while the sample was saturated with nitrogen

and later CO₂ and finally water, using an effective pressure of 25 MPa. The sample was vacuumed for at least 12 hours prior to changing the fluid saturant. Experiments were set up such that velocities and strains could be measure during the various CO₂ phase changes possible during well-site injection (e.g. liquid to gas, liquid to supercritical) by varying related pressures and temperatures appropriately. A more detailed explanation of the experimental procedure and equipment can be found in Yam (2011).

During the heating and cooling isobaric CO₂ run (Confining pressure = 31 MPa; Pore pressure = 6 MPa), it was observed that the rate of temperature change has a strong effect on the specific temperature at which the expected phase change would occur. As the density of the saturant has a strong effect on the elastic properties and, therefore, the observed velocities in the sample it is useful to consider the properties of CO₂ for this particular run (Figure 1). Two possible explanations for this disparity include: 1) the transport of CO₂ into (during condensation) and out of (during precipitation) the sample during the phase transition; and 2) the time-dependent heat transfer out of (during condensation) and into (during evaporation) the sample. As the pore-pressure is maintained, the heat transfer within the sample, and between the sample and the surrounding fluid, seems most critical. In particular, the temperature measured during each run is the temperature of the confining fluid, measured within ~5 cm of the top of the sample assembly. As such, the recorded temperature will not necessarily represent the temperature throughout the sample assembly; unless it is given time to equilibrate. To determine an approximate equilibration time at each temperature, and help explain the observed phase transition lag, a lumped capacitance method was applied (Wendl, 2005) to model the approximate thermal transient state within the material upon an otherwise rapid external temperature change in the confining fluid. This model assumes that temperature gradients within the materials are negligible.

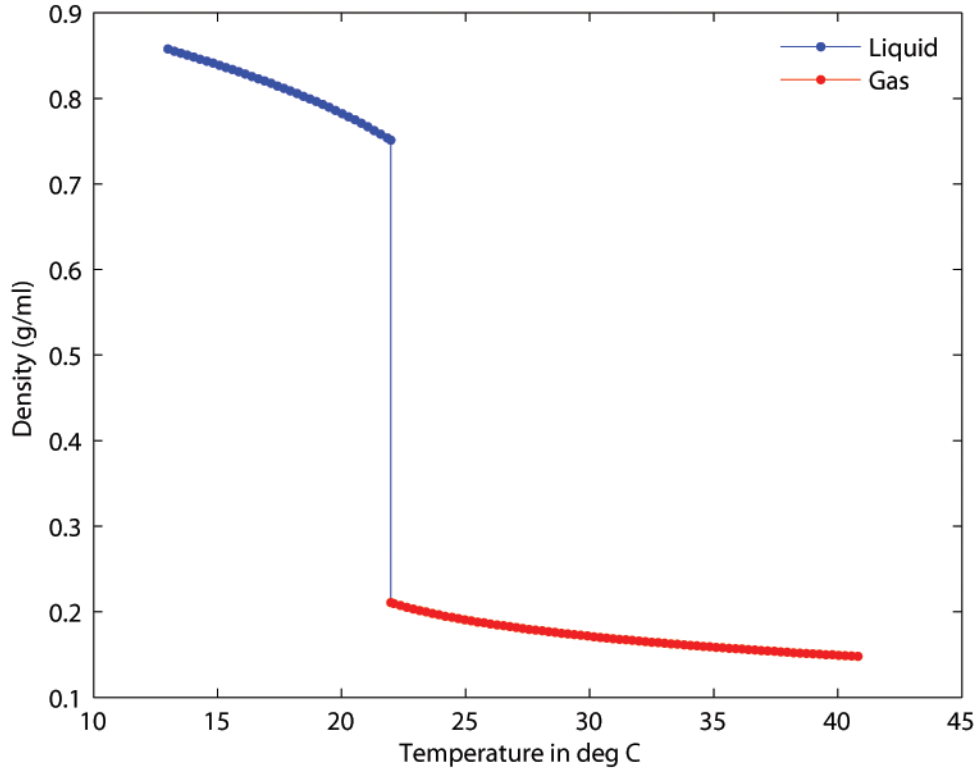


Figure 1: A diagram presenting the density of CO₂ as a function of temperature at constant pressure (6 MPa). The phase change is clearly evident as a sharp drop in density. The liquid to vapor phase change occurs at ~22 °C (NIST website).

Lumped capacitance method:

It is a relatively simple and special case where the temperature in the solid is spatially invariant, i.e. temperature gradients are negligible, $T(r, t) \approx T(t)$ and $T(0) = T_i$. This analysis, known as the lumped capacitance model, assumes that the convective resistance between the boundary of the solid and its surroundings is larger than the conductive resistance of energy transfer in the solid. The energy balance equation can be written by considering only the convective energy transfer at the boundary of the conductor.

The overall energy balance is:

$$\dot{q}_{in} = \dot{q}_{stored} \quad (1)$$

where $\dot{q}_{in} = hA_s(T(t) - T_\infty)$ is the rate of heat transfer into solid and the rate of increase of heat energy of the solid is $\dot{q}_{stored} = \rho c_p V dT/dt$. This yields the following:

$$\rho c_p V \frac{dT}{dt} = hA_s(T_\infty - T(t)) \quad (2)$$

and

T = Maximum temperature

t = Time

$T(t)$ = Time dependent temperature

ρ = Density of the sample in kg/m^3

c_p = Specific heat capacity of the sample in $\text{J/kg} \cdot \text{K}$

h = Heat transfer coefficient of fluid (oil) to solid in $\text{W/m}^2\text{K}$

V = Volume of the sample = $\pi r^2 H$

A_s = Area of the sample = $2\pi r H$

r = Radius of the cylindrical sample in meters (m)

H = Height of the sample in meters (m)

Equation (2) can be rewritten as:

$$\frac{T(t)-T}{T_0-T} = \exp\left(-\frac{hA_s}{\rho c_p V} t\right) \quad (3)$$

where T_0 is the initial temperature of the conductor.

Therefore, temperature changes take the form of a simple exponential as spatial gradients are small enough to be neglected.

$$\frac{T(t)-T}{T_0-T} = e^{-t/\tau} \quad (4)$$

Where:

$$\tau = \text{Time constant} = \frac{\rho c_p V}{hA_s}$$

$$\rho c_p V = \text{Thermal capacitance}$$

$$1/hA_s = \text{Convection thermal resistance}$$

From equation (4), the temperature of a solid as a function of time becomes:

$$T(t) = T_\infty + (T_0 - T_\infty)e^{-t/\tau} \quad (5)$$

Therefore, the time needed to heat a sample from T_0 to a target temperature T is:

$$t = \frac{\rho c_p V}{hA_s} \ln \frac{T_\infty - T_0}{T_\infty - T} \quad (6)$$

and the total energy transferred over some period of time can be written as:

$$Q = hA_s \int_0^t \theta dt = T - T(t)$$

which gives

$$Q = \rho c_p V \theta_0 (1 - e^{-t/\tau}) \quad (7)$$

where $\theta_0 = T - T_0$

The model holds if the Biot number is $Bi = hr/2k \ll 1$ (k = Thermal conductivity).

Sample calculation:

Here a sample, having a temperature of $T_0 = 15$ °C, is placed in a bath having a temperature of 45 °C. Using this model we can calculate the time, t , required for the sample to reach a temperature $T = 25$ °C and determine the approximate amount of time required to reach equilibrium with the bath.

Given that:

$$h = k/L_c = 2k/r = 2 \times 1.5/0.0127 = 24 \text{ W/m}^2\text{K}$$

where L_c is the characteristic length. The thermal resistance to heat transfer from the sample is due to the dielectric layer (the tubing isolating the sample from the hydraulic fluid) and the convection coefficient. That is

$$R = \frac{l}{k_p} + \frac{1}{h} = \frac{0.00635}{0.19} + \frac{1}{24} = 0.0751 \text{ m}^2\text{K/W}$$

So the convection coefficient for the sample and tubing is $U = 1/R = 13.32 \text{ W/m}^2\text{K}$

and the effective Biot number is $Bi = UL_c/k = Ur/2k = 13.32 \times 0.0127/2 \times 8 = 0.0105$.

Since $Bi < 0.1$, the lumped capacitance model is applicable. Replacing h in equation (6) with U , yields:

$$t = \frac{\rho c_p V}{UA_s} \ln \frac{T_\infty - T_0}{T_\infty - T}$$

where:

$$V = \pi r^2 H = \pi \times 0.0127^2 \times 0.0515 = 2.61 \times 10^{-5} \text{ m}^3$$

$$A_s = 2\pi r H = 2 \times \pi \times 0.0127 \times 0.0515 = 0.0041 \text{ m}^2$$

$$\rho = 3750 \text{ kg/m}^3$$

$$c_p = 800 \text{ J/kg.K}$$

Resulting in:

$$t = 581.34 \text{ sec} = 9.689 \text{ min}$$

So the time required for the sample to reach 25 °C is ~9.7 minutes. The time required for the sample to reach equilibrium with the bath is roughly 2 hours (Figure 2).

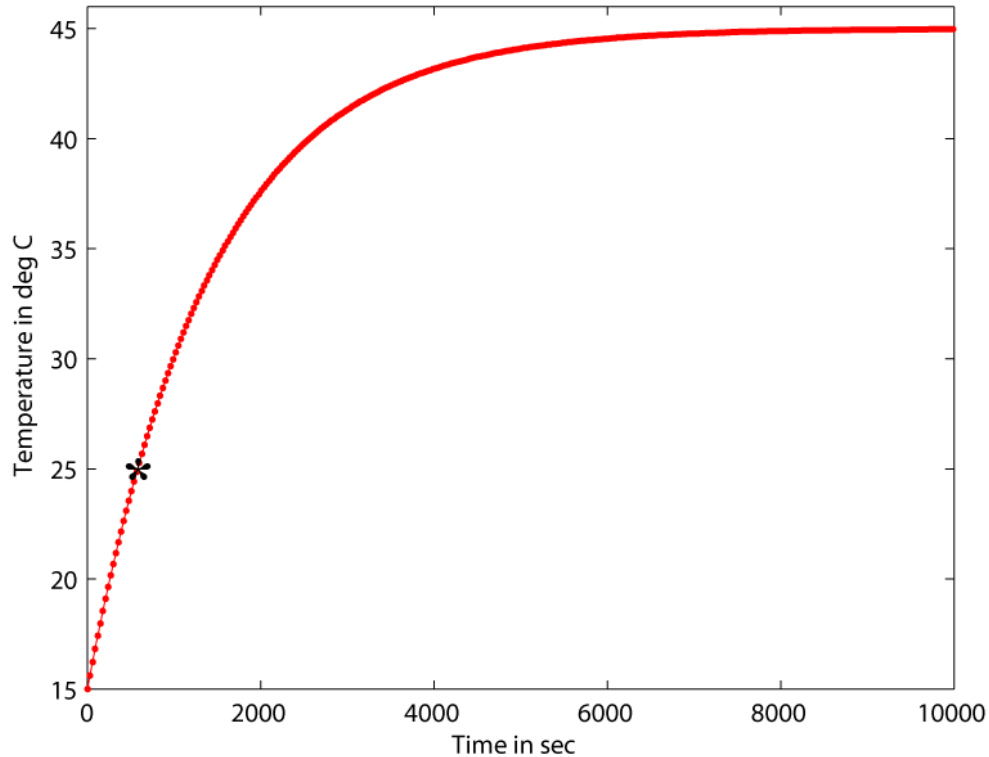


Figure 2: A plot of the time required for a sample at 15 °C to equilibrate with a surrounding fluid at 45 °C based on the lumped capacity model. The black asterisk represents the results of the sample calculation. The time required to reach equilibrium is not dependant on the temperature differential. Note that this calculation is only intended to be a rough estimation.

Examples

The following plots are included to provide some details observed with the synthetic sample (Figure 3 and 4). They also provide clear evidence of the lag observed during the liquid-to-gas and gas-to-liquid CO₂ phase transition during a series of isobaric heating and cooling runs (Figure 4). For the sake of brevity, only the P-wave data are provided. The first plot (Figure 3) illustrates the stiffness of the dry sample. Essentially, there is very little change in the measured P-wave velocities or hysteresis outside experimental uncertainty, clearly emphasizing the effect of CO₂ saturation. It is worth noting that in both the heating and cooling runs, the flow-rate of the CO₂ into (during cooling) and out of (during heating) increased significantly immediately prior to the observed velocity changes, but appeared to remain relatively low and stable during the velocity changes.

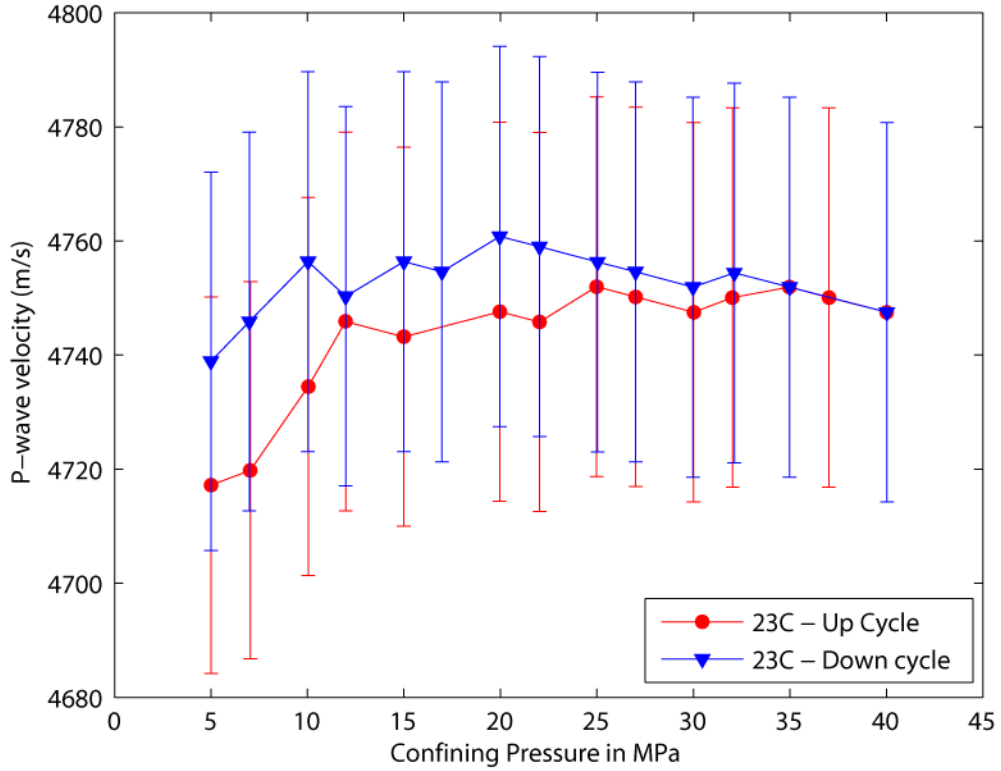


Figure 3: The room-temperature dry run reveals that P-wave velocities do not change significantly with varying confining pressure and constant temperature. The S-wave data provides similar results. The hysteresis between the pressurization and depressurization cycles reflects the effect of pressure on the sample porosity.

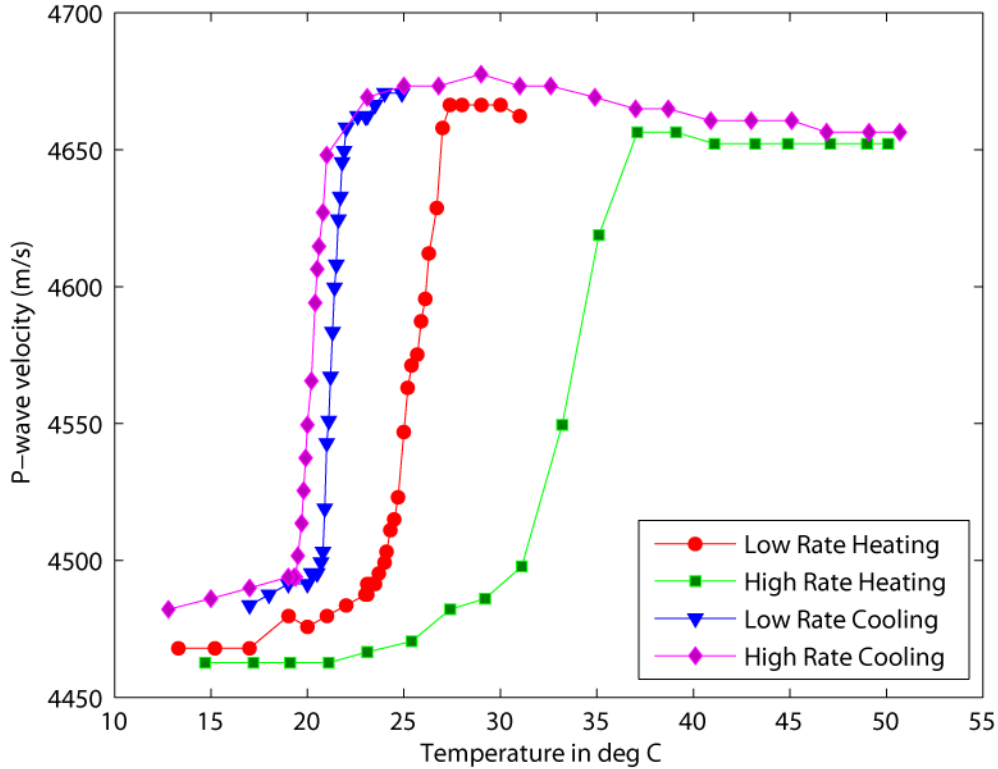


Figure 4: The P-wave velocities for the CO₂ saturated sample as a function of temperature show the influence of the rate of heating and cooling on the temperature at which the phase change occurs. It is clear that the gas-to-liquid phase change (cooling) is not as strongly influenced by the cooling rate as the liquid-to-gas phase change (heating). The heating runs show a significant variation in both slope and temperature. The approximate rates are as follows: High Rate Heating: ~2.5 min/°C; High Rate Cooling: ~5 min/°C; Low Rate Heating: ~20 min/°C; Low Rate Cooling: ~20 min/°C. The expected phase transition of pure, isolated CO₂ under these conditions is ~22 °C (NIST website).

Conclusions

As efforts to sequester CO₂ in subsurface reservoirs increases, the ability to effectively monitor storage sites during and following injection should be a high priority. In addition to other techniques, the ease and affordability of deploying seismic arrays to monitor such sites over extended time-frames make it an attractive option. To improve the results of seismic surveys, knowledge of the physical properties of the reservoir rocks under *in situ* conditions is essential. Workers must continue to improve their ability to measure these properties. These recent results suggest that care must be taken when conducting ultrasonic measurements of CO₂ samples saturated when phase transitions are involved. Detailed modeling can be an effective means to mitigate these issues and determine the optimum parameters at

which experiments should be conducted. And, while this paper deals specifically with a synthetic sample, the principals can be instructive for future work with natural reservoir rocks.

Acknowledgements

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