Velocity and density of water with dissolved CH_4 and CO_2

De-hua Han and Min Sun, RPL, University of Houston*

Summary

We have investigated velocity and density of degassed water (H_2O) with dissolved CH_4-CO_2 in temperature ranged from 25°C to 200°C and pressure ranged from 20MPa to 138MPa. Pressure effect shows the same trends as that on degassed water. Temperature effect on velocity of water with dissolved CO_2 shows a minor modification: dissolved CO_2 causes an increase of velocity when temperature is lower than 60°C, but a decrease of velocity with higher temperature. With more dissolved CO_2, the temperature effect on velocity appears to increase. Higher GWR also causes a higher density. The effect of GWR on density tends to decrease with increasing temperature. Velocity of degassed water can be decreased by saturated CH_4 about 1~2 %, which can be ignorable, and by saturated CO_2 about 5%, which may be resolvable seismically. Preliminary models have been developed to predict velocity and density of H_2O-CH_4-CO_2 miscible mixtures.

Introduction

As CO_2 sequestration becomes a major operation to reduce greenhouse effect, we have observed increased effort to inject CO_2 into underground reservoirs including into near completed hydrocarbon reservoirs, which can also enhance (residual) oil recovery (EOR). Ideally, CO_2 should be stored in the reservoir for hundreds or more years to come. However, due to complicated reservoir structure, flow unit distribution and seal condition, no one can sure: how is CO_2 distributed? How reliable is the processing in storage of CO_2 for years to come? We need to carefully monitor injected CO_2 in reservoirs.

Water is a major component of pore fluid. However in near complete reservoir environment (low pressure and may fill more gas) with injected CO_2, we have to concern how hydrocarbon gas (CH_4) and CO_2 can be pressurized to dissolve into water. However, that gases dissolve into water is a complicated processing. For example, amount of dissolved gas and gas-water phase equilibrium are controlled by distribution of gas-water contact, time, and solubility at in situ condition. Can the processing alter the seismic properties of water significantly? Without answer, the question will affect our ability to monitor.

In this investigation we focus on velocity and density of water partially saturated with CO_2 for GWR (volume ratio of gas and water at the standard condition, 15.56 ºC and 1 atm pressure) 25L/L and 35L/L, temperature from 25°C (77° F) to 150°C (302° F), and pressure from 20.69 MPa (3,000 psi) to 103.44 MPa (15,000 psi). And we also give preliminary models for H_2O-CH_4-CO_2 miscible mixtures.

Experimental design

The experiments were designed to measure velocity and density of distilled water with various gas contents at in situ temperature and pressure conditions. The measurement is limited to liquid phase only, which is either fully or partially saturated with gas. Previously we have measured velocities of water with fully dissolved CH_4 gas and CO_2 respectively (Han and Sun, 2008). In this study, we prepared two new samples with controlled, dissolved CO_2 for velocity and density measurement.

1. water with dissolved CO_2 as GWR 25 L/L.
2. water with dissolved CO_2 as GWR 35 L/L.

The CO_2 with purity > 99.5% was obtained from commercial sources.

Experimental result and analysis

Water properties

We applied the International Association for the Properties of Water and Steam-Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam (IAPWS-IF97; Wagner and Kruse, 1998) and FLAG program (a computer program developed by the Fluids/DHI consortium) to calculate velocity and density of water. We also used it as a standard to calibrate the experiment system. Figure 1 shows the measured data of distilled water and calculated values. The system accuracy for velocity is 0.25% and density 0.1%.
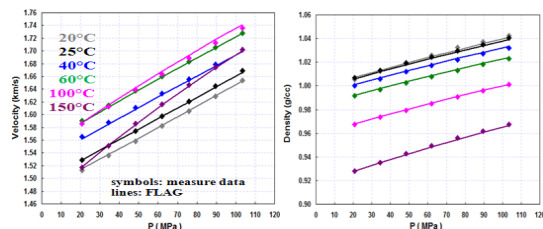
Velocity and density of water with dissolved CH_4 and CO_2

Figure 1. Calibrated experimental system for velocity and density measurement.

Solubility of CH_4 and CO_2 in water

CO_2-water solubility is a measure of the maximum amount of dissolved CO_2 into water which can be counted by saturated GWR with given pressure and temperature condition. With CO_2 phase equilibrium with water, amount of gas dissolved in water depends on solubility at temperature and pressure conditions. Therefore, at in situ, amount of gas dissolved into water can vary in wide range, but is bounded by solubility or called as bubble condition. In this study, we have measured single phase water with controlled amount of dissolved CO_2 with varied P & T conditions. It means that CO_2 in water is in under-saturated conditions. If we can assume that GWR is a main control to affect the velocity of water, then we can ignore effect of the saturation condition. In this way, velocity can be used to evaluate GWR. If gas phase coexists with water, the solubility can be used to calculate the GWR. Based on the GWR, we can calculate water velocity, which can be used to calibrate measured velocities at in situ.

We used Duan's model (Duan, 2003) to estimate CO_2's solubility which can work in the temperature ranged from 0 to 263°C, and pressure from 0 to 200 MPa with overall uncertainty of 7%. For solubility of methane, we used a methane solubility correlation developed by McCain, which agrees well with their experimental data (Spivey et al., 2004).

Measured velocity

The measured data show the effect of pressure, temperature and GWR. Due to low solubility, velocity and density trends of the water are not modified significantly with dissolved gas.

1. Velocity of H_2O with dissolved CO_2

Velocities as function of pressure and temperature for two water samples with GWR 25 and 35 L/L are presented in Figure 2.
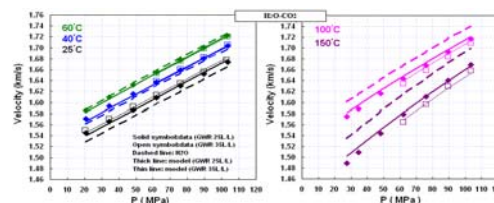

Figure 2. Measured velocities of H_2O-CO_2 mixtures with deferent GWRs with model predicted result.

In comparison with velocity of degassed water as shown by the dashed lines, there are some notable features of H_2O-CH_4-CO_2 miscible mixtures:
1. Velocity increases with increasing pressure but maintains almost the same gradient as that of degassed water.
2. Velocities show abnormal temperature effect similar as that of degassed water. With increasing temperature, velocities increase to their maximum around 70°C and then decrease.
3. Dissolved CO_2 shows a complicated effect on velocity at different temperature ranges. At 25 ℃, dissolved CO_2 increases velocity of degassed water (<2%). The higher the GWR is, the higher the velocity becomes. This effect seems to increase with decreasing pressure. But the effect is reduced with increasing temperature and diminishes around 60 ℃. However, at high temperature, dissolved CO_2 shows reverse effect to reduce velocity (<4%). The higher the GWR, the lower the velocity. This effect reduces velocity more with decreasing pressure. The missed data of 35L/L sample are below the bubble point where T > 40℃ and P< 69 MPa.

The above observation is consistent with the measured velocity data on CO_2-saturated water in 2008. Within the measured ranges, from 34.48 MPa (5,000 psi) up to 103.44 MPa (15,000 psi), and temperature from 23° C (73.4° F) to 150° C (302°F), the maximum of the velocity decrease caused by saturated CO_2 is around 70 m/s (~5%) at the high temperature and high pressure end (where the solubility of CO_2 is about 45L/L) (Figure 3).

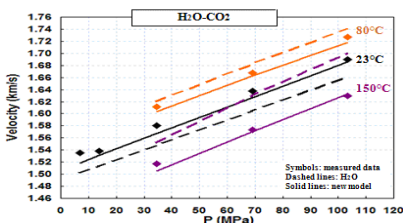# Velocity and density of water with dissolved CH₄ and CO₂

Figure 3. Measured velocities of CO_2 saturated water with model predicted result.

2. Velocity of H₂O with dissolved CH₄

Comparing to solubility of CO_2, CH_4 has much smaller solubility in water, which diminishes its effect on velocity. We measured velocities of CH_4-saturated water for years since 2001. Measured conditions extended from 68.96 MPa (10,000 psi) up to 137.92 MPa (20,000 psi), and 25°C (77°F) up to 200°C (392°F) (Han and Sun, 2008). The result shows that dissolved CH_4 causes a decrease of velocity of water, but which is less than 2% (Figure 4).
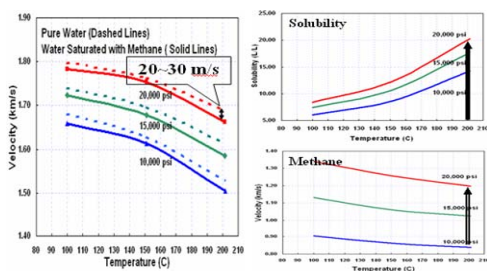

Figure 4. Measured velocities of CH_4 saturated water.

Measured density

Figures 5 shows measured densities of H_2O- CO_2 mixture with CO_2 GWR of 25L/L and 35L/L respectively. Density of water with dissolved CO_2 increases with pressure and GWR, decreases with temperature, and increases with GWR. The CO_2 effect tends to reduce slightly with increasing temperature.

Modulus can be obtained from the measured velocity and density as shown in Figure 6. Because of the small deviations of velocity and density from those of degassed

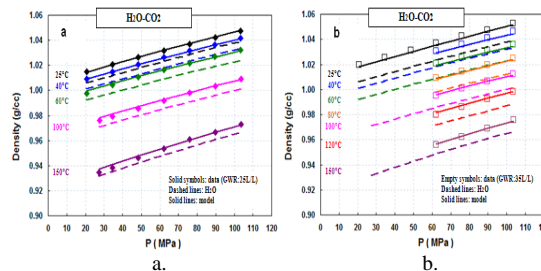water, the moduli have the same trends as velocity of degassed water.

Figure 5. Measured densities of H_2O-CO_2 mixture with model predicted values: a. the sample with 25L/L; b. the sample with 35L/L.
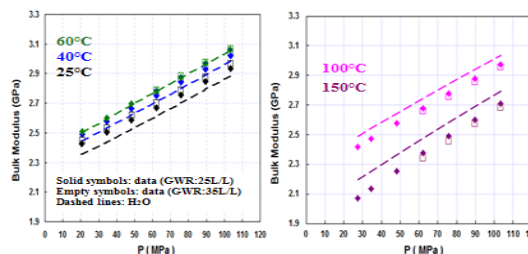

Figure 6. Modulus of water with dissolved CO_2 for GWR 25L/L and 35L/L.

Modeling for H₂O-CH₄-CO₂ mixture

Based on the experimental result, we develop preliminary models for predicting velocity and density of H_2O-CH_4-CO_2 mixture within experimental conditions. Considering that properties of water still dominate properties, we use the water model and give corrections for gas effect. An empirical model is proposed as,

$$F = F_{H_2O} + f_{CO_2}C_{CO_2} - f_{CH_4}C_{CH_4} \cdot \qquad (1)$$

Here, F is property of H_2O-CH_4-CO_2 mixture, F_{H_2O} is property of pure water, f_{CO_2} and f_{CH_4}, C_{CO_2} and C_{CH_4}, are the volume fractions and correlations of CO_2 and CH_4, respectively. The volume fractions are normalized by total gas volume counted as GWR.

$$f_{CO_2} = \frac{GWR_{CO_2}}{GWR_{CO_2}+GWR_{CH_4}} \text{ and } f_{CH_4} = \frac{GWR_{CH_4}}{GWR_{CO_2}+GWR_{CH_4}} \cdot \qquad (2)$$

GWR_{CO2} and GWR_{CH4} are CO_2-water and CH_4-water ratio in L/L, respectively.

Velocity and density of water with dissolved CH₄ and CO₂

Velocity model

$$V = V_{H_2O} + f_{CO_2} C_{CO_2\_v} - f_{CH_4} C_{CH_4\_v} \qquad (3)$$

Here, V_{H_2O} is velocity of water in km/s.

$$C_{CO_2\_v} = S_v T_v \qquad (4)$$

S_v is a correlation of velocity correction with dissolved CO_2,

$$S_v = GWR_{CO_2} / 28 \qquad (5)$$

T_v is a correlation of velocity correction with temperature in the second order polynomial,

$$T_v = aT^2 + bT + c \qquad (6)$$

Where T is temperature in degree C, and

$$a = 0.0000014770636$$
$$b = -0.0006626486993$$
$$c = 0.0287180206334$$

C_{CH4_v} is for velocity correction with dissolved CH_4,

$$C_{CH_4\_v} = GWR_{CH_4} \qquad (7)$$

Density model

$$\rho = \rho_{H_2O} + f_{CO_2} C_{CO_2\_\rho} - f_{CH_4} C_{CH_4\_\rho} \qquad (8)$$

Here, ρ_{H2O} is density of water.

$$C_{CO_2\_\rho} = S_\rho T_\rho \qquad (9)$$

S_ρ is a correlation of density correction with CO_2's solubility in water, and is the same as for velocity correction,

$$S_\rho = GWR_{CO_2} / 28 \cdot \qquad (10)$$

T_ρ is a correlation of density correction with temperature in third order of polynomial,

$$T_\rho = aT^3 + bT^2 + cT + d \qquad (11)$$

Where a = -0.00000000620048
b = 0.00000158708
c = - 0.00013630062072
d = 0.01224855899828

$C_{CH_4\_\rho}$ is for density correction with dissolved CH_4. We still need data to refine its formula.

Comparing with the measured data as shown in Figure 2, 3 and 5, the predicted values of the velocity model for the H_2O-CH_4 and H_2O-CO_2 mixtures are matched within the experimental conditions. The predicted values of the density model for H_2O-CO_2 are also matched data well. But we still need to test and refine them for density of H_2O-CH_4

mixture, and for velocity and density of H_2O-CH_4-CO_2 mixture.

For a given solubility, the maximum of velocity deviation can be estimated by simply adding both effects of CO_2 and CH_4 linearly. Actual effect will be smaller if considering interaction among water, CH_4, and CO_2. This is also the maximum effect on brine, because gas solubility will decrease with increasing salinity (Batzle and Wang, 1992).

Conclusions

The dissolved CH_4-CO_2 gas has small effects (in a few percent) on velocities of water, mainly due to low solubility of gas in water, especially for hydrocarbon gas (CH_4).

However, we have observed detailed and systematic CO_2 effect, which is interesting and may be significant with high resolution data at in situ.

1. At low temperature of 25°C, dissolved CO_2 causes an increase velocity (< 1.5%). However, this GWR effect is reduced with increasing temperature and diminished at around 60°C. Then CO_2 effect on velocity of water reversed: reducing water velocity with increasing GWR, and increasing temperature.
2. Dissolved CO_2 on water systematically increases density of water. However, CO_2 effect on density tends to reduce slightly with increasing temperature.

The maximum effect of dissolved CH_4 reduces velocity of water about 1 ~ 2 %, which is ignorable. The maximum effect of dissolved CO_2 to reduce velocity can only occur at high temperature (>60°C) and the maximum reduction of water velocity is about 5%, which could be significant for filed observation seismically.

Preliminary models can be used to estimate velocity and density of H_2O-CH_4-CO_2 mixture, although they need more data to refine.

Acknowledgements

EDITED REFERENCES

Note: This reference list is a copy-edited version of the reference list submitted by the author. Reference lists for the 2013 SEG Technical Program Expanded Abstracts have been copy edited so that references provided with the online metadata for each paper will achieve a high degree of linking to cited sources that appear on the Web.

REFERENCES

Batzle, M., and Z. Wang, 1992, Seismic properties of pore fluids: Geophysics, **57**, 1396–1408.

Duan, Z. and R. Sun, 2003, An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar: Chemical Geology, **193**, 257–271.

Han, D., and M. Sun, 2008a, CO_2 velocity measurement and modified model for temperatures down to – 10 °C and up to 200°C: Presented at the Annual Meeting of Fluids, DHI.

Han, D., and M. Sun, 2008b, Velocity of water saturated with methane at temperatures up to 200°C and pressures up to 138 MPa: Presented at the Annual Meeting of Fluids, DHI.

Span, R., and W. Wagner, 1991, A new equation of state and tables of thermodynamic properties for methane covering the range from the melting line to 625 K at pressures up to 1000 MPa: Journal of Physical and Chemical Reference Data, **25**, no. 6.

Spivey, J. R., J. McCain, and R. North, 2004, Estimating density, formation volume factor, compressibility, methane solubility, and viscosity for oilfield brines at temperatures from 0 to 275C, pressures to 200 MPa, and salinities to 5.7 mole/kg: Journal of Canadian Petroleum Technology, **43**, no.7.