Thermodynamic Tools for Modeling of Subsurface Hydrogen Storage: An Integrated Approach Using Gassmann Fluid Substitution and the BWRS Equation of State

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Background

Modeling seismic responses in reservoir rocks is crucial for effective hydrogen (H_2) storage for several reasons. It provides essential information about the reservoir's capacity, integrity, and behavior under various conditions, which is crucial for operational efficiency and environmental safety:

1. Fluid Density Determination: Understanding the density of hydrogen within the reservoir is essential. Density variations can indicate the presence and concentration of hydrogen, which is vital for assessing the storage capacity and stability of the reservoir. Seismic waves are sensitive to changes in density, and accurate models help interpret these variations correctly.
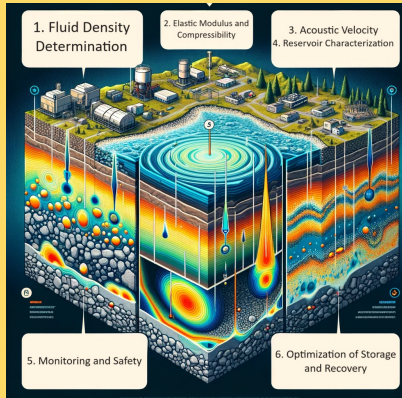
2. Elastic Modulus and Compressibility: The reservoir rock's elastic modulus (or its reciprocal, the adiabatic compressibility) is a crucial parameter influencing how seismic waves propagate through the medium. Accurate measurements of these properties allow a better understanding of the rock's ability to store hydrogen without compromising its structural integrity. It also helps predict how the rock will respond to changes in pressure and temperature, which are common in H_2 storage scenarios.

3. Acoustic Velocity: The speed at which seismic waves travel through the rock (acoustic velocity) is directly influenced by fluids like hydrogen. By accurately modeling this velocity, it's possible to infer the saturation and distribution of hydrogen within the reservoir. This information is critical for planning extraction processes and monitoring the storage site's integrity over time.

4. Reservoir Characterization: Accurate seismic modeling helps in detailed reservoir characterization. It allows geologists and engineers to create a clearer picture of the subsurface, identifying potential storage zones, barriers, and pathways for hydrogen migration.

5. Monitoring and Safety: Continuous monitoring of seismic responses can provide real-time data on the condition of the reservoir, helping to ensure the safety and efficiency of hydrogen storage. It can detect any changes or anomalies that might indicate issues, such as leaks or structural weaknesses in the reservoir.

6. Optimization of Storage and Recovery: By understanding the seismic properties of the reservoir, it becomes possible to optimize the storage and recovery processes, ensuring maximum efficiency and minimal environmental impact.

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Biot-Gassmann theory (Gassmann 1951)

It is extensively used for modeling velocity changes in rocks undergoing fluid substitution and used to calculate the effective bulk modulus of the rock (K_e).

$$K_e = K_{dry} + n^2 K_f \Big/ \left[\varphi + \frac{K_f}{K_g}(n - \varphi) \right]$$

Where, dry bulk modulus (K_{dry}) is generally determined experimentally from velocity measurements on a dry sample. The Biot effective stress coefficient (n) is determined using static (Biot, 1956) or dynamic (Todd and Simmons, 1972) measurements depending on the type of loading or measurement acquired. φ is the total connected porosity of the sample. K_f is the modulus of fluid mixture which comprises one or more fluids (such as brine, oil, H_2 etc.) in pore space and is calculated from the Ruess average of the bulk modulus, K and concentration S.

$$K_f = 1 \Big/ \sum_{i=1}^{n} \left(\frac{S}{K} \right)_i \Rightarrow \frac{1}{K_f} = \frac{S_w}{K_{brine}} + \frac{S_{H_2}}{K_{H_2}} \& \begin{cases} S_w \left(= 1 - S_{H_2}\right) \\ \rho_f = S_w \rho_{brine} + S_{H_2} \rho_{H_2} \end{cases}$$

The mineral bulk modulus (K_g) is the Voigt-Ruess-Hill (VRH) average of moduli of each minerals. The VRH is calculated as:

$$K_{VRH} = \frac{1}{2} \left(K_{Ruess} + K_{Voigt} \right) \& K_{Ruess} = \sum_{i=1}^{n} \left(\frac{C}{K_m} \right)_i \& K_{Ruess} = \sum_{i=1}^{n} C K_{m_i}$$

C is the volumetric concentration and Km is the modulus of the respective minerals. This theory can only be applied if the associated assumptions are not violated. The rock should be homogeneous, isotropic and non-reactive to pore fluid.

Furthermore, all the pore space is connected, and deformations are sufficiently slow to allow pore pressure equilibration throughout the fluid. A complete tutorial for applying Biot Gassmann theory is given in Smith et al. (2003). Domenico (1976) compared the experimental and theoretical predicted velocities as a function of brine saturation. He observed a steep increase in velocity after 90% brine saturation. There is a good match of predicted S wave velocity with its theoretical counterpart.

Hill (1963), Berryman and Milton (1991) proposed correlation for '*Patchy saturation*' to estimate effective bulk modulus, K_e:

$$K_e = \left(\sum_{i}^{n} \frac{f_i}{K_{isat} + \frac{4}{3}G} \right)^{-1} - \frac{4}{3}G$$

Where, f_i represents volumetric fraction of ith patch, n is the number of patches, G is the shear modulus, K_{sat} is the bulk modulus of the rock saturated with ith fluid. The predicted velocities are calculated from

$$V_p = \sqrt{\frac{K_e + \frac{4}{3}G}{\rho_{bulk}}} \quad \& \quad V_s = \sqrt{\frac{G}{\rho_{bulk}}}$$

The bulk density for fluid saturated rock is calculated as

$$\rho_{bulk} = \rho_g (1 - \varphi) + \rho_f \varphi$$

BWRS Equation of state and its extension for H_2

Benedict-Webb-Rubin-Starling Equation of State (BWRS-EoS) is a Non-Cubic equation:

$$p = \rho RT + \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \rho^2$$
$$+ \left(bRT - a - \frac{d}{T} \right) \rho^3 + \alpha \left(a + \frac{d}{T} \right) \rho^6$$
$$+ \frac{c\rho^3}{T^2} (1 + \gamma \rho^2) \exp(-\gamma \rho^2)$$

The equation of state expression for the fugacity has the form

$$RT \ln f = RT \ln(\rho RT) + 2 \left(B_0 RT - A_0 - \frac{C_0}{T^2} + \frac{D_0}{T^3} - \frac{E_0}{T^4} \right) \rho$$
$$+ \frac{3}{2} \left(bRT - a - \frac{d}{T} \right) \rho^2 + \frac{6\alpha}{5} \left(a + \frac{d}{T} \right) \rho^5$$
$$+ \frac{c}{\gamma T^2} \left(1 - \left(1 - \frac{1}{2} \gamma \rho^2 - \gamma^2 \rho^4 \right) \exp(-\gamma \rho^2) \right)$$

For a multi component system, mixing rule by Bishnoi and Robinson (1972) are adopted to calculate the values of mixture properties in EoS:

$$B_0 = \sum_i x_i B_{0_i}$$
$$A_0 = \sum_i \sum_j x_i x_j A_{0_i}^{1/2} A_{0_j}^{1/2} (1 - k_{ij})$$
$$C_0 = \sum_i \sum_j x_i x_j C_{0_i}^{1/2} C_{0_j}^{1/2} (1 - k_{ij})^3$$
$$\gamma = \left(\sum_i x_i \gamma_i^{1/2} \right)^2$$
$$b = \left(\sum_i x_i b_i^{1/3} \right)^3$$
$$a = \left(\sum_i x_i a_i^{1/3} \right)^3$$
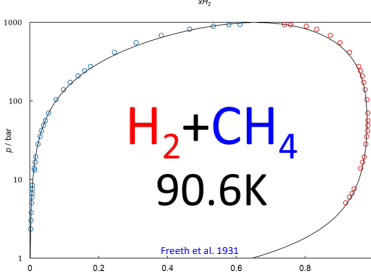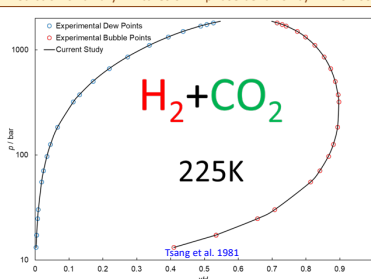$$\alpha = \left(\sum_i x_i \alpha_i^{1/3} \right)^3$$
$$c = \left(\sum_i x_i c_i^{1/3} \right)^3$$
$$D_0 = \sum_i \sum_j x_i x_j D_{0_i}^{1/2} D_{0_j}^{1/2} (1 - k_{ij})^4$$
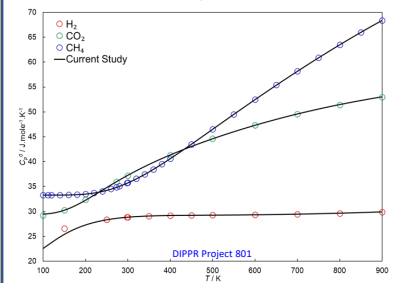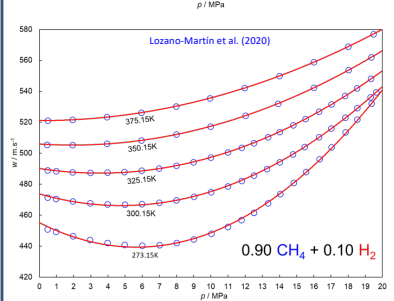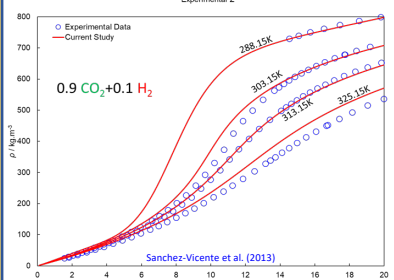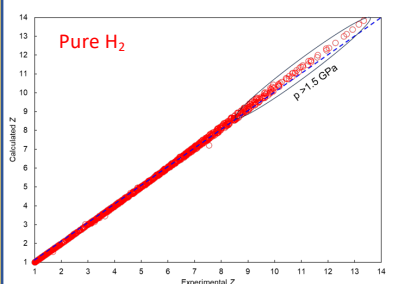$$d = \left(\sum_i x_i d_i^{1/3} \right)^3$$
$$E_0 = \sum_i \sum_j x_i x_j E_{0_i}^{1/2} E_{0_j}^{1/2} (1 - k_{ij})^5$$

Prediction of binary mixtures of H_2 phase behavior by BWRS-EoS

$H_2 + CO_2$
225K
Tsang et al. 1981

$H_2 + CH_4$
90.6K
Freeth et al. 1931

The performance of a model in predicting the volumetric properties of pure H_2 and its mixtures

The performance of a model in predicting the volumetric properties of pure H_2 and its mixtures is a complex issue that depends on the model's type, the quality and comprehensiveness of the training data, the specific properties and mixtures being considered, and the balance between accuracy and computational efficiency. Continuous validation and adaptability to new data are also crucial for maintaining high performance.

Pure H_2
p >1.5 GPa

0.9 CO_2+0.1 H_2
288.15K
303.15K
313.15K
325.15K
Sanchez-Vicente et al. (2013)

Lozano-Martín et al. (2020)
375.15K
350.15K
325.15K
300.15K
273.15K
0.90 CH_4 + 0.10 H_2

H_2
CO_2
CH_4
Current Study
DIPPR Project 801

Conclusion

It highlights that model performance in predicting the volumetric properties of hydrogen relies on factors like the model type, data quality, and a balance between accuracy and computational efficiency. Crucial to effective hydrogen storage is seismic response modeling, which provides insights into fluid density, elastic modulus, compressibility, and acoustic velocity, all vital for assessing reservoir capacity and integrity. The application of the Biot-Gassmann theory is significant in this context, especially for modeling velocity changes in rocks and calculating the effective bulk modulus. The mineral bulk modulus (Kg) calculation, following the Voigt-Ruess-Hill (VRH) average, is applicable under specific conditions such as homogeneity and isotropy of the rock. Additionally, the Benedict-Webb-Rubin-Starling Equation of State (BWRS-EoS) plays a key role in predicting hydrogen's phase behavior in pure and mixtures. It underscores the need for continuous validation and adaptability of models to ensure operational efficiency and environmental safety in hydrogen storage.

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