Supplementary file

Interfacial dynamics and mass transfer in underground hydrogen storage applications: A review of H_2 flow, stability and storage performance

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Underground hydrogen storage (UHS) shares fundamental concepts with underground natural gas storage (UGS), allowing UHS projects to leverage existing UGS experience in site selection, technology, monitoring, and operational cycles (Kanaani et al., 2022). Despite this shared foundation, a key challenge for UHS arises from hydrogen's lower volumetric energy density, which necessitates a significantly larger storage volume to achieve energy capacity equivalent to methane. This disparity is primarily attributed to the distinct physicochemical properties of hydrogen (P.J. Linstrom and W.G. Mallard), as visually summarized in Fig. S1.

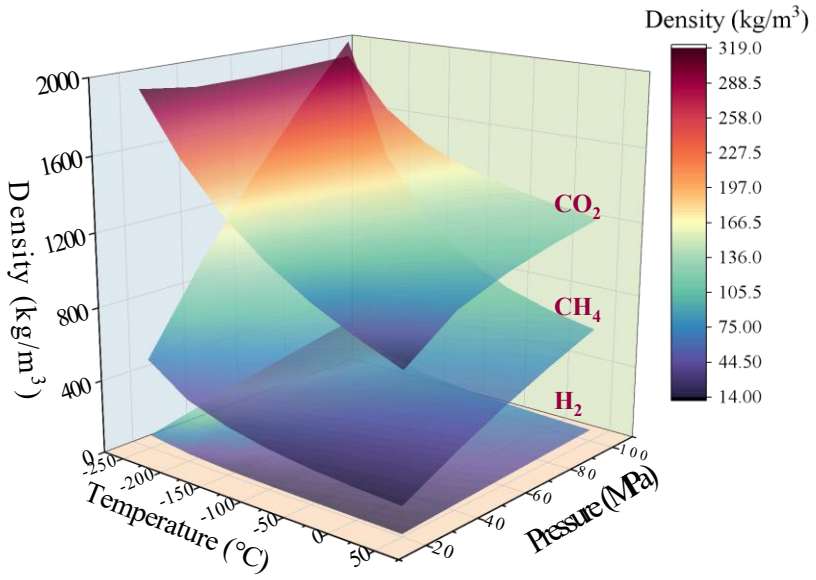

Fig. S1. Storage density of gas under certain pressure and temperature conditions (Tarkowski et al., 2021; Cachadiña et al., 2022; Thiyagarajan et al., 2022; Cai et al., 2024).

Comparative H_2-N_2 displacement studies indicate that H_2 exhibits superior drainage efficiency and can restore nearly 100% of its original gas saturation, unlike N_2, which retains higher residual water saturation under the same conditions (Al-Yaseri et al., 2022). Numerical modeling in low-permeability sandstone showed that lateral H_2 diffusion is governed by porosity and permeability, which are determined by the pore-throat structure of rock. At high flow rates, viscous forces drive H_2 into smaller pores, forming preferential pathways that reduce H_2 saturation at breakthrough and limit effective storage capacity (Bagheri et al., 2023; Wang et al., 2024).

Specifically, hydrogen exhibits a high diffusion rate, leading to a greater leakage risk compared to geological CO_2 storage and underground natural gas storage (Xiong et al., 2025). The diffusion rate of H_2 is primarily governed by porosity, pore connectivity, and the effective molecular diffusion coefficient， and the equation can be expressed as (Boving and Grathwohl, 2001; Thiyagarajan et al., 2022)：

$$D_e = (D_f \phi c)/\tau^2 \quad (1)$$

where D_e is the effective diffusion coefficient, D_f is the free molecular diffusion coefficient, ϕ is porosity, c is the constrictivity factor, and τ is tortuosity. The conversion of H_2 to CH_4 and H_2S at the caprock interface or within the reservoir via diffusion can significantly impact storage efficiency and requires careful evaluation. The geo-methanation process, which converts H_2 and CO_2 into CH_4, offers a promising approach for renewable energy storage. (Hellerschmied et al., 2024) demonstrated through simulated reservoir ecosystems experiments that H_2 and CO_2 can be reproducibly converted to CH_4 over 14 cycles spanning 357 days.

Depleted oil and gas reservoirs show substantial potential for trans-seasonal H_2 storage, particularly when CO_2 is used as cushion gas, enabling large-scale geologic methanation. These formations offer enormous storage capacity, with European depleted gas fields providing approximately an order of magnitude greater storage resources than oil fields. However, further research is needed to evaluate potential reactions between residual oil and H_2 in such reservoirs (Le Gallo, 2024).

The primary source of H_2S in UHS systems comes from the conversion of SO_4 ions or sulfate/sulfide minerals dissolved in brine. (Wilhelm et al., 1977) found that H_2S exhibits significantly higher water solubility than CH_4 under low-pressure conditions (at 25°C and 1 atm, molar fraction is 18.51×10^{-4} for H_2S versus 0.2507×10^{-4} for CH_4). Generated gaseous H_2S can dissolve in brine to form aqueous species including H_2S, HS^-, and S^{2-}, thereby reducing its gas-phase concentration. To ensure storage safety and efficiency, potential reactions between H_2 and other reservoir components must be carefully considered. Unfavorable biological or mineralogical reactions can be effectively minimized through optimized reservoir temperature and pressure control, along with appropriate reservoir type selection.

Although CH_4 demonstrates markedly higher adsorption capacity than H_2, the adsorption isotherm of pure H_2 remains largely unaffected by variations in rock wettability (Abid et al., 2022; Mirchi and Dejam, 2023). The adsorption process can be modeled using the Langmuir isotherm (Wang et al., 2023; Shang et al., 2024):

$$n = (n_L P)/(P + P_L) \quad (2)$$

where n is the gas adsorption capacity per unit sample mass at a pressure P, n_L is the maximum Langmuir adsorption capacity, and the Langmuir pressure P_L (MPa). The absolute and excess adsorption amounts are related by (Wang et al., 2023; Shang et al., 2024):

$$m_{ex} = m_{abs} - \rho(T,P)V_f \quad (3)$$

where m_{ex}, m_{abs} are the excess and absolute adsorption amounts of H_2, with $\rho(T,P)$ as its density at given T and P, and V_f as the pore system's free volume. Therefore, pressure is the dominant factor governing adsorption

capacity, with higher pressures significantly increasing the amount of adsorbed H_2 and enhancing storage potential. In contrast, elevated temperatures reduce adsorbed H_2, which is unfavorable for storage efficiency. Claystone exhibits significant adsorption potential, particularly in samples with high specific surface area and a high volume of pores below 30 nm, though storage density remains limited (Wang et al., 2023). Salt rock is considered an excellent sealing or storage medium due to its extremely low permeability and self-healing capacity, although tectonic deformation may induce fracturing and compromise containment integrity (Li et al., 2023). Shale, while being an effective seal against gas leakage, has low porosity and permeability, resulting in poor injectivity and recovery efficiency. In fact, it maintains structural integrity only under specific thermo-mechanical conditions (Yekeen et al., 2022).

The interplay between salinity and interfacial properties controls H_2 migration and trapping, manifested in the distinct size distribution of H_2 clusters under varying H_2-brine flow ratios (Fig. S2). The heterogeneous H_2 cluster distributions under imbalanced flow conditions (Fig. S2, top) visually corroborate these dynamics.

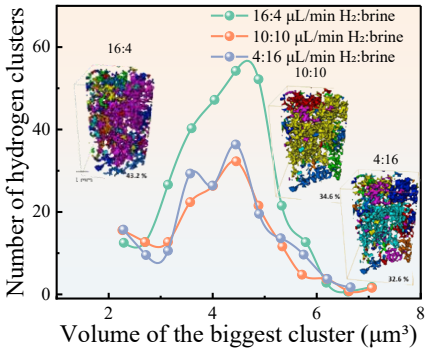

Fig. S2. H_2 saturation and cluster volume injected for different flow rates (Thaysen et al., 2023).

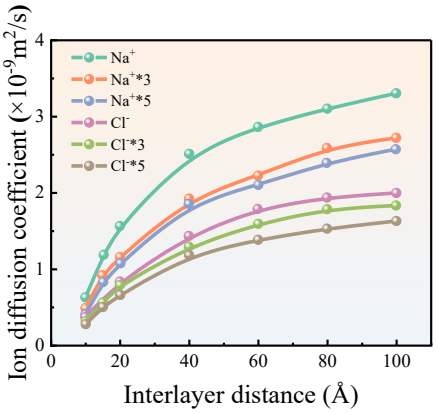

Fig. S3. Interlayer distance in nanopores at different concentrations (Hamed Mashhadzadeh and Faroughi, 2025).

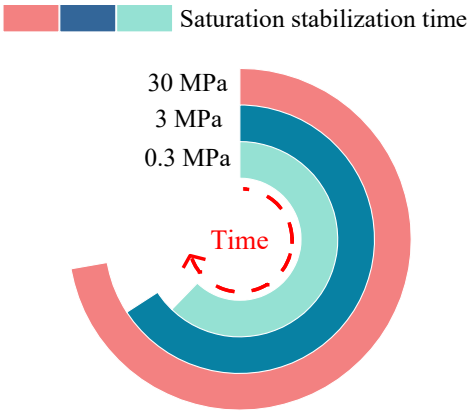

Fig. S4. Saturation versus dimensionless time at different pressures (Bagheri et al., 2023).

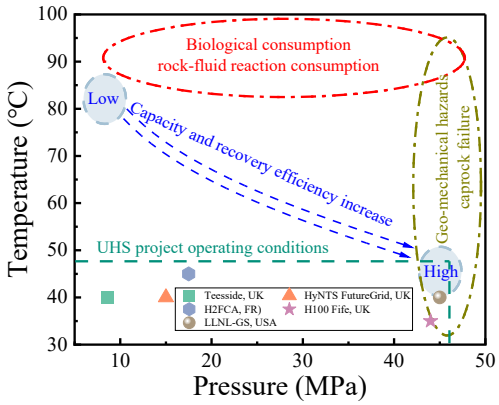

Fig. S5. Synergistic effects of temperature and pressure.

In geochemical terms, pH and pE (redox potential) critically govern reservoir integrity and H_2 stability. Although H_2 has a limited direct effect on pH, its presence creates a strong reducing environment, facilitating the reduction of electron acceptors like SO_4^{2-} and Fe^{3+} (Hassannayebi et al., 2019; Heinemann et al., 2021; Tremosa et al., 2023), with models predicting the reductive dissolution of minerals such as barite and pyrite (Jacquemet, 2021). Operational strategies should be tailored to reservoir lithology to mitigate these effects.

Table S1 Key factors affecting UHS performance.

Factor	Key parameters and trends	Impact on UHS	Reference
Geochemistry (pH and pE)	-High H_2 concentration leads to reducing environment (negative pE) -May increase pH via redox reactions	-Governs reservoir integrity and H_2 stability -Induces mineral alteration and H_2S production	(Ganor et al., 1995; Jacquemet, 2021; Alhamad et al., 2023; Tremosa et al., 2023; Zeng et al., 2023)
Salinity and ionic composition	-High salinity increases brine density and viscosity -Specific ions affect adsorption and dissolution (Fig. S3) -$CaCl_2$/$MgCl_2$ brines more favorable than NaCl	-Reduces reservoir permeability and H_2 flow (Fig. S2) -Affects H_2 IFT, migration, and trapping -Influences H_2 cluster formation (Fig. S2, top)	(Muhammed et al., 2022; Rezaei et al., 2022; Muhammed et al., 2023; Li et al., 2024)
Interfacial tension (IFT)	-Decreases with increasing temperature and pressure -H_2-brine IFT higher than CH_4 or CO_2 systems -Enhanced by salinity	-Controls H_2 distribution, capillary trapping, and multiphase flow -Lower IFT favors H_2 penetration and distribution	(Young, 1805; Esfandyari et al., 2022) (Hosseini et al., 2022b; Alanazi et al., 2023)
Pressure (P)	-Optimal range: ~5–20 MPa (Fig. S5) -Increased P enhances H_2 adsorption capacity, compresses pores, may open microfractures -Decreased P increases leakage risk, shortens breakthrough time (Fig. S4)	-Directly affects storage density, leakage risk, and pore structure -Pressure depletion during withdrawal causes gas cluster expansion and seepage-like flow	(Zivar et al., 2021; Raza et al., 2022; Tarkowski and Uliasz-Misiak, 2022; Al-Yaseri et al., 2023; Alms et al., 2023; Bagheri et al., 2023; Dokhon et al., 2024; Malki et al., 2024)
Temperature (T)	-Optimal Range: ~10–50°C (Fig. S5) -Increased T significantly reduces IFT, causes thermal rock expansion	-Enhances molecular motion, reduces IFT -Affects porosity/permeability via thermal expansion	(Liebscher et al., 2016; Panfilov, 2016; Hosseini et al., 2022a; Davoodi et al., 2025)
Diffusion and transport	-Sensitive to salinity/composition gradients	-Governs H_2 transport, mixing, and potential leakage	

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