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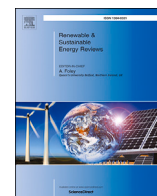
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Mechanistic controls on hydrogen migration, trapping, and recovery in porous reservoirs

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HIGHLIGHTS

- Cross-scale synthesis links flow, geochemistry, and microbiology under cyclic UHS.
- Hydrogen endpoint k_{r,H_2} , is 0.003–0.083, about 10× below CO₂-brine while Brooks-Corey exponents $n_g \approx 3 - 10$ for H₂ vs. 1.6–1.8 for sc-CO₂.
- Hydrogen combines unfavourable mobility ratio with high gravity number, where cyclic hysteresis reduces recoverable H₂ fraction to 16–25%.
- *FZI* links pore-network architecture to deliverability and storage security, with standardized benchmarking needed to resolve inter-study discrepancies.

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ABSTRACT

Underground hydrogen storage (UHS) in geological formations is increasingly recognized as a cornerstone of low-carbon energy systems, offering large-scale, long-duration buffering to stabilize variable energy supply. Its feasibility in porous reservoirs such as saline aquifers and depleted hydrocarbon fields depends on coupled multiphase flow and biogeochemical processes, yet substantial uncertainty remains regarding the ability of porous media to sustain cyclic injection-withdrawal while preserving storage integrity, injectivity, and gas purity. Hydrogen displacement is controlled by relative permeability, residual trapping, gas redistribution, and pore-scale instabilities such as snap-off and capillary fingering, and advances in high-pressure microfluidics, micro-computed tomography, and interfacial characterization now enable direct observation of these processes. Compared with CO₂ and CH₄, hydrogen shows distinct interfacial behaviour, with endpoint $k_{r,H_2} \approx 0.003\text{--}0.083$ (about an order of magnitude below CO₂-brine baselines) and fitted Brooks-Corey gas-phase exponents $n_g \approx 3\text{--}10$ against $\approx 1.6\text{--}1.8$ for supercritical CO₂, and with storage performance further dependent on wettability, mineralogy, viscosity, and flow history. Hydrogen-rock wettability is not uniformly strongly water-wet but varies with mineralogy, organic content, and microbial activity, and salinity effects on contact angle are reported but not universal. Microbially mediated wettability alteration, together with mineral dissolution and secondary precipitation, can further modify porosity, permeability, and capillary behaviour under cyclic loading. A significant gap nonetheless remains between homogeneous laboratory conditions and the heterogeneity of real reservoirs, where the transition to rate-sensitive regimes critically affects gas connectivity and trapping, and where current models often neglect rate-dependent, microbially mediated, and pore-scale redistribution processes that evolve dynamically under cyclic operation. This review connects previously siloed treatments of diffusion, multiphase flow, geochemistry, and microbiology through a cross-scale, process-coupled framing of cyclic injection-withdrawal, and identifies standardized side-by-side benchmarking on identical lithologies as the methodological step needed to resolve the inter-study contradictions and to support multiscale, rate-sensitive predictive frameworks for safe, efficient, and scalable UHS deployment.

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1. Introduction

Hydrogen, generated through diverse pathways including renewable energy sources and subsurface natural hydrogen generation, has attracted growing attention as a versatile, non-emissive energy carrier with the potential to decarbonize energy, industrial, as well as transportation sectors [99,119,147,148]. This positions hydrogen as a critical asset in the global transition toward a cleaner, more sustainable, and low-carbon energy future, particularly for energy infrastructures dominated by intermittent renewable sources, where supply and demand are mismatched over daily to seasonal timescales [91]. Addressing these mismatches requires large-scale, long-duration energy storage solutions capable of buffering variability beyond the temporal limits of conventional storage technologies.

Surface-based hydrogen storage methods (such as compression, liquefaction, and chemical storage) remain constrained by high costs, limited storage capacities, and short discharge durations, typically ranging from hours to several days (Fig. 1a, [82,144,185]). As a result, underground hydrogen storage (UHS) has emerged as a promising long-duration energy storage alternative (Fig. 1a), offering capacities from gigawatt-hours to terawatt-hours and discharge times extending from days to months [152,176]. Historical precedents as listed in Table S1 demonstrate the technical feasibility of large-scale subsurface hydrogen storage. For example, the Kiel storage project in Germany stored town gas containing ~62% hydrogen during the 1960s and 1970s before transitioning to natural gas storage [138,209]. More recently, hydrogen storage initiatives, including AquaPort (Hamburg) and HyPSTER (France), among others listed in Table S1, are advancing UHS toward pilot and commercial deployment.

Among potential geological storage options (Fig. 1b, see *Supplementary Text*), salt caverns, saline aquifers, and depleted hydrocarbon reservoirs are widely regarded as the most viable candidates for UHS due to their large storage capacities and favourable economics compared to surface tanks [91,190,209]. These storage options differ markedly in geological properties, storage capacity, geographic distribution, and technological maturity, each imposing distinct constraints on flow behaviour and containment mechanisms (cf. Table S2). Salt caverns, for example, offer excellent containment owing to their extremely low permeability and self-healing properties. In these systems, multiphase flow is largely confined to the wellbore and near-cavern regions, and long-term containment risks are minimal [93,176]. In contrast, porous media storage relies on a combination of structural trapping, capillary sealing, and pressure management within laterally extensive reservoirs, where hydrogen migration, buoyancy-driven segregation, and residual trapping govern storage performance [47,142,190,209]. These fundamental differences strongly influence which physical and chemical processes dominate system behaviour, as well as the scales over which they operate [100,119].

Porous media reservoirs are particularly attractive for UHS because they can leverage existing infrastructure and decades of operational experience from natural gas storage and geological carbon dioxide (CO₂) sequestration, including established practices for site characterization, pressure management, and containment assessment [20,91,114,182]. However, despite these analogies, the direct transferability of existing storage frameworks is limited. The physicochemical and hydrodynamic behaviour of hydrogen differs fundamentally from that of methane (CH₄) and CO₂ (Fig. 1b), requiring a re-evaluation of storage concepts, operational strategies, and risk assessment methodologies [100,119].

These limitations arise from hydrogen's distinct properties, as its low viscosity and molecular weight enhance its mobility and buoyancy, promoting viscous instabilities, rapid plume migration, and enhanced mixing with residual or cushion gases during cyclic injection and withdrawal [100,119]. Hydrogen's relatively high diffusivity compared to CH₄ and CO₂ further amplifies molecular transport, increasing the potential for migration along pre-existing fractures or faults and raising concerns related to leakage, hydrogen-induced fracturing, and material

embrittlement [62,110,209]. Beyond flow-related effects, hydrogen interacts with the subsurface environment through a range of physicochemical and biogeochemical processes (Fig. 1c). Microbial activity may consume hydrogen and generate by-products such as H₂S and CH₄ [4,62], while geochemical reactions can alter porosity, permeability, and compromise caprock properties, ultimately affecting storage performance and recoverable gas quality [7,202]. Unlike CO₂ sequestration, which targets permanent containment, UHS requires repeated injection-withdrawal cycles to meet fluctuating energy demand, introducing additional geoscientific and operational complexity [176,186,209].

Despite rapidly growing interest in UHS, most studies remain confined to laboratory-scale experiments, numerical simulations, and pilot projects, and a clear pathway to widespread commercial deployment is still emerging. This gap reflects the fragmented treatment of the processes that collectively govern hydrogen behaviour in geological reservoirs, including multiphase flow, geochemical reactions, microbial activity, and geomechanical responses. Recent studies have provided valuable insights into hydrogen mobility, phase behaviour, reactivity, and interactions with reservoir rocks and formation fluids [4,32,79,85], while complementary review articles (cf. Table S3) have synthesized advances in diffusion, solubility, interfacial phenomena, and biogeochemical transformations. However, these advances have largely been scale dependent and developed as silos, limiting the emergence of unified insights into system-scale storage performance.

The performance of UHS is often governed by a hierarchy of coupled processes operating across spatial and temporal scales [91,176,209]. Although geological storage systems are inherently multi-physical, not all processes exert equal control at all times. At operational timescales relevant to injection, withdrawal, and short shut-in periods, storage behaviour is primarily controlled by multiphase flow processes, which dictate injectivity, pressure evolution, breakthrough timing, residual trapping, and working gas recovery [85,100,119]. Most experimental and numerical investigations conducted to date implicitly operate within this flow-dominated regime, often neglecting longer-term biogeochemical evolution [32,79]. Over longer residence times and repeated injection-withdrawal cycles, physicochemical processes increasingly influence system evolution. Hydrogen dissolution, mineral reactions, surface chemistry-driven wettability alteration, and microbially mediated hydrogen consumption can progressively modify pore structure, interfacial properties, and fluid composition [4,7,62]. Although these processes are often slow relative to operational flow dynamics, their cumulative effects may alter permeability, capillary pressure relationships, and recovery efficiency. These changes in turn modify multiphase flow behaviour and progressively blur the distinction between flow-dominated and chemistry-dominated regimes. This framework provides the basis for organizing the literature reviewed herein.

The relative importance of these controls is strongly scale-dependent, further complicating the interpretation and integration of existing studies. At the pore scale, interfacial forces and mineralogical heterogeneity govern phase distribution and trapping mechanisms, whereas at the core and reservoir scales these effects are upscaled into effective relative permeability, capillary pressure, and hysteresis relationships that control large-scale storage performance [32,79,85,100]. Apparent discrepancies among experimental, pore-scale, and reservoir-scale studies therefore frequently arise not from contradictory physics, but from differences in the dominant processes resolved at each scale and the assumptions used to represent unresolved behaviour. As a consequence, significant uncertainties remain regarding the ability of saline aquifers and depleted oil and gas reservoirs to sustain repeated injection-withdrawal cycles while maintaining storage integrity, withdrawal efficiency, and gas purity suitable for end-use applications [80]. Divergent findings across laboratory, field-scale, and modelling studies underscore persistent knowledge gaps related to fluid-rock interactions, microbial consumption pathways, geochemical alteration, and geomechanical stability, all of which collectively govern the long-term viability of UHS systems.

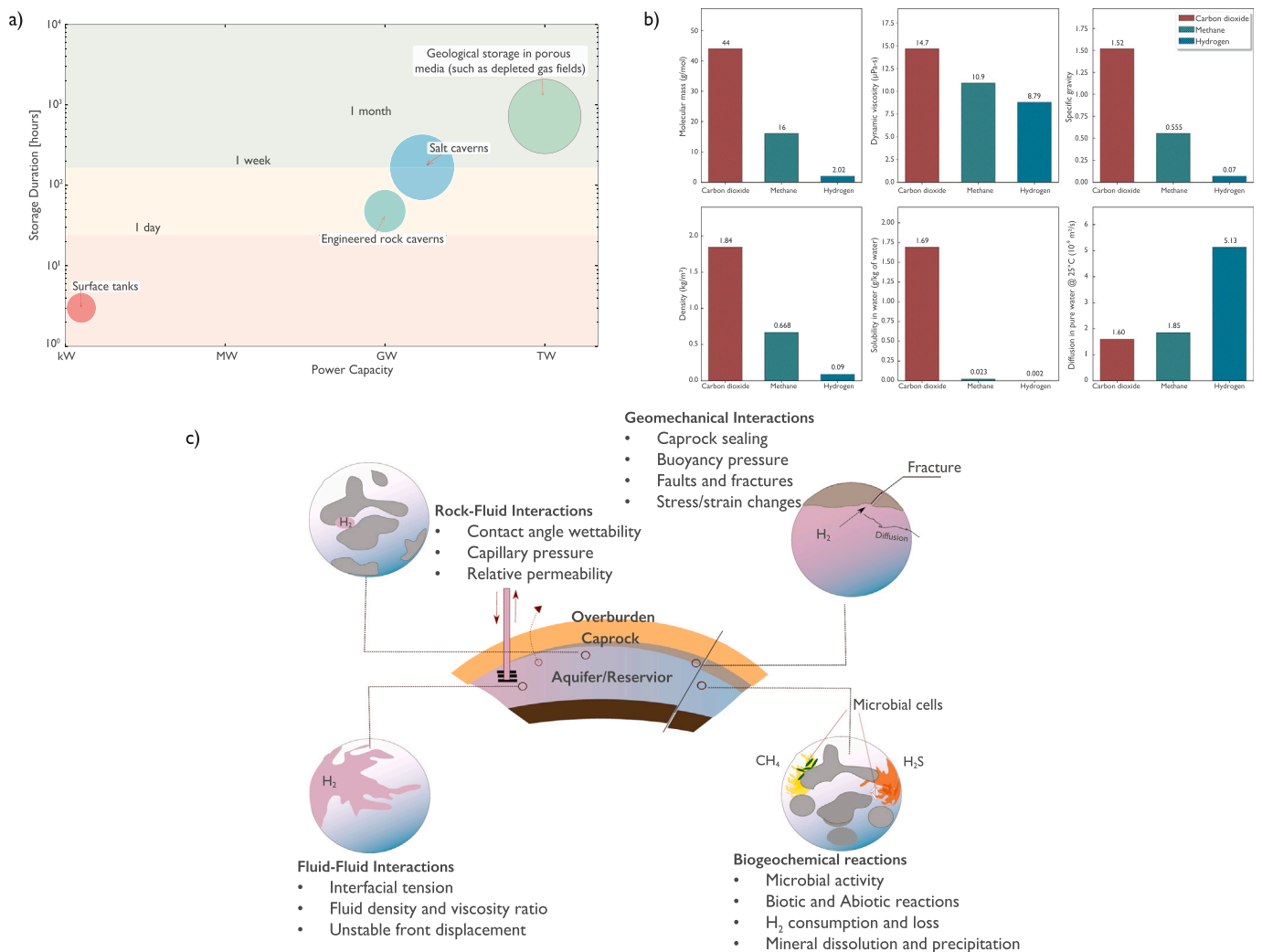


Fig. 1. (a) Hydrogen storage technologies compared by power duration and capacity, including surface tanks, engineered rock caverns, salt caverns, and porous subsurface reservoirs. Geological storage provides the largest capacities and longest durations. (b) Comparison of key physicochemical properties of CO₂, CH₄, and H₂, showing that H₂ has the lowest density, viscosity, and solubility, but the highest diffusivity, shaping its distinct subsurface behaviour. (c) Conceptual illustration of H₂ behaviour in subsurface reservoirs: injected H₂ displaces reservoir fluids and rises until it reaches an impermeable caprock, where it spreads laterally and becomes trapped. Storage performance is influenced by rock-fluid properties, microbial consumption, geochemical reactions, caprock integrity, and fluid dynamics. Together, the panels link the system-level motivation for UHS to the gas properties and coupled subsurface processes that distinguish hydrogen from more conventional storage gases.

To address these challenges, this review adopts a concept-driven synthesis organized around two dominant but interacting control regimes. First, multiphase flow-dominated studies are reviewed to examine the roles of wettability, capillarity, pore structure, trapping mechanisms, hysteresis, and cyclic injection-withdrawal dynamics in controlling hydrogen storage capacity and recovery efficiency. Second, physicochemical studies are reviewed to assess the impacts of geochemical, microbial, and coupled reactive processes on reservoir evolution, gas quality, and long-term storage integrity. The distinctive contribution of this review is therefore not to provide another single-process inventory, but to connect these previously separated literatures through the integrative question of how hydrogen migration, trapping, and recovery evolve during cyclic storage in porous reservoirs. In contrast to hydrodynamic-focused reviews (Table S3, e.g., [2,110,155,164]), we treat molecular transport as one component of time-dependent gas redistribution that interacts with capillary trapping, Ostwald ripening, and cushion-gas mixing, rather than as an isolated process. Similarly, in contrast to multiphase-flow-focused reviews (Table S3, e.g., [90,91,157,200]), we explicitly consider how interfacial physics is modified by mineralogy, brine chemistry,

microbial activity, and long residence times. In contrast to geochemical, microbiological, and caprock-integrity reviews (Table S3, e.g., [35,62,69,165,196]), we evaluate chemical and biological reactions in terms of their feedback on wettability, pore structure, gas quality, injectivity, and recoverability. This cross-scale, process-coupled perspective is used to identify when UHS behaviour is flow dominated, when physicochemical feedback becomes important, and where current data and models fail to bridge pore-scale observations with reservoir-scale design. By synthesizing studies across spatial and temporal scales within this unified framework, the review clarifies process dominance, reconciles divergent observations, and highlights critical uncertainties that must be addressed to advance UHS design and operation.

2. Multiphase flow-dominated controls on underground hydrogen storage

The development of UHS as a large-scale, low-carbon energy buffer requires a clear understanding of how hydrogen migrates and becomes retained in brine-saturated reservoirs. Hydrogen injection results

in an immiscible multiphase flow system in which capillary, viscous, and gravitational forces interact across scales to control plume evolution, trapping mechanisms, and thus recovery efficiency [41,136,177]. The balance among these forces determines whether hydrogen propagates as a stable displacement front, bypasses significant pore volumes via preferential flow paths, or becomes immobilized as disconnected ganglia.

At the reservoir scale, the primary challenge in UHS is gravity-driven hydrogen segregation. Due to its low density, hydrogen is highly buoyant in brine-saturated systems, promoting its upward migration and preferential invasion into the upper portions of the storage unit, followed by extensive lateral spreading along the reservoir top [113]. This gravitational behaviour can reduce sweep efficiency and limit the effectively accessible storage volume. In parallel, the strong viscosity contrast between hydrogen and formation brine can promote viscous instabilities. When low-viscosity hydrogen displaces higher-viscosity brine, the displacement front may become unstable and develop fingering, leading to early hydrogen breakthrough and leaving substantial portions of the reservoir unswept [31,191,193].

At the formation or bedding scale, spatial variability in capillary entry pressure results in capillary barriers that either locally trap hydrogen or divert the plume into preferential flow pathways [151,174,205]. The localized trapping zones and non-uniform saturation distributions will in turn affect injectivity and recoverability. For example, Bo et al. [39] demonstrated that macro-scale heterogeneity can reduce storage efficiency by up to 15.8% over a decade of cyclic hydrogen injection and withdrawal. At the pore space, capillary-controlled processes such as snap-off and bypassing can immobilize hydrogen as disconnected ganglia, giving rise to residual trapping and saturation hysteresis. Elevated capillary entry pressures hinder hydrogen invasion into smaller pore throats, increasing the fraction of gas that becomes irreversibly trapped [4,7,18,40]. A recent study by Peng et al. [150] further confirms that capillary effects exert strong control on hydrogen plume evolution and trapping across a range of flow rates.

Across these scales, multiphase flow behaviour is governed by the balance among viscous, capillary, and gravitational forces. These competing effects are commonly quantified using dimensionless groups that characterize displacement efficiency, flow stability, and buoyancy-driven segregation. The balance between viscous and capillary forces is expressed through the capillary number (Ca),

$$Ca = \frac{\mu v}{\gamma} \quad (1)$$

where μ is the dynamic viscosity of the displacing fluid (Pa s), v is the superficial velocity of the displacing phase ($v_D = Q/A$, m s^{-1}), and γ is the hydrogen-brine interfacial tension (IFT) (N m^{-1}). This distinction is important when comparing experiments across media with different porosities because using the interstitial velocity ($v_p = v_D/\phi$) rather than v_D changes the reported Ca by a factor of the inverse porosity ($1/\phi$). Low values of Ca indicate capillary-dominated displacement, which promotes trapping and saturation heterogeneity, whereas increasing Ca allows viscous forces to progressively overcome capillary resistance and improve displacement efficiency. The stability of the displacement front is further governed by the endpoint mobility ratio,

$$M = \frac{k_{r,g}^{\text{end}}/\mu_g}{k_{r,w}^{\text{end}}/\mu_w} \quad (2)$$

where $k_{r,g}^{\text{end}}$ and $k_{r,w}^{\text{end}}$ are the endpoint relative permeabilities of the gas and aqueous phases, respectively (cf. Section 2.2). Values of $M > 1$ correspond to an unfavourable mobility contrast that promotes viscous fingering and unstable displacement fronts. Considering representative hydrogen-brine values of $k_{r,g}^{\text{end}} \sim 0.05$ and $k_{r,w}^{\text{end}} \sim 0.5$ yields $M \sim 5$ –10, indicating a strong tendency toward the viscous instabilities observed during hydrogen injection [31,193]. Buoyancy-driven segregation is

quantified through the gravity number:

$$N_g = \frac{k \Delta \rho g}{\mu v} \quad (3)$$

where k is the absolute permeability, $\Delta \rho$ is the density difference between water (ρ_w) and gas (ρ_g), and g is the gravitational acceleration. Hydrogen's exceptionally low density gives a large $\Delta \rho$ which, combined with its low viscosity, places it in a high- N_g regime in which gravitational forces dominate viscous drag and favour upward migration and lateral spreading beneath the caprock [91,113]. Coupled with the reduced gas relative permeability characteristic of hydrogen-brine systems (cf. Section 2.2), these properties produce a combination of moderate-to-high Ca , unfavourable M , and high N_g , a coupling that is uncommon among other storage gases, and promotes capillary trapping, displacement instability, and buoyancy-driven segregation. Understanding how these competing forces interact therefore forms the basis for predicting hydrogen migration and recovery in subsurface reservoirs.

Among these controls, interfacial tension plays a particularly important role because it governs capillary forces and forms the basis for both capillary-pressure relationships and wettability-driven displacement processes. Interfacial tension (γ) represents the energy per unit area required to maintain the interface between two immiscible fluids and reflects the intermolecular forces acting at the fluid-fluid boundary. In hydrogen-brine systems, γ controls the ability of hydrogen to displace brine from pore spaces and therefore exerts a strong influence on residual trapping, capillary entry pressure, and displacement efficiency [31,102,116]. The significance of γ extends beyond the gas-liquid interface, as the interaction of hydrogen and brine with the rock introduces additional interfacial energies at the gas-solid and liquid-solid boundaries. The balance among these interfacial energies is described by the contact angle, θ , as illustrated by Young's equation

$$\cos \theta = \frac{\gamma_{s-\text{H}_2} - \gamma_{s-\text{brine}}}{\gamma_{\text{H}_2-\text{brine}}} \quad (4)$$

where $\gamma_{\text{H}_2-\text{brine}}$ is the hydrogen-brine IFT, and $\gamma_{s-\text{H}_2}$ and $\gamma_{s-\text{brine}}$ are the solid-hydrogen and solid-brine IFT, respectively. Wettability, often used interchangeably with contact angle, determines which phase preferentially adheres to the mineral surface. Low contact angles ($\theta < 90^\circ$) indicate water-wet (water adheres to minerals) conditions and high contact angles ($\theta > 90^\circ$) result in gas-wet (gas adheres to minerals) conditions. As a result, wettability governs capillary entry pressures, pore occupancy, and displacement pathways. Many reservoir rocks are strongly water-wet, which prevents hydrogen invasion into smaller pores, limiting it to larger pores and well-connected pathways. However, exposure to hydrocarbons or surface treatments can shift wettability toward intermediate- or gas-wet conditions, lowering capillary barriers and altering trapping behaviour [4,18]. UHS is also inherently cyclic, and the alternating injection and withdrawal processes induce hysteresis in relative permeability and capillary pressure, which can enhance residual trapping through repeated drainage-imbibition sequences [7,40,82,204]. These dynamic multiphase flow interactions and the controlling petrophysical parameters are constrained through constitutive relationships that link pore-scale forces to large-scale behaviour [37,106].

Therefore, the long-term viability of UHS depends critically on resolving these multiphase flow dynamics under representative subsurface conditions. Addressing this challenge requires targeted experimental investigation of wettability, interfacial tension, capillary pressure, relative permeability, and hysteresis, which provide the essential inputs for robust process prediction and risk assessment.

2.1. Wettability, interfacial tension, and capillary control

A central challenge of UHS in porous media is the immobilization of hydrogen within subsurface pore spaces. Under the low capillary numbers characteristic of UHS operations, multiphase hydrogen flow is

dominantly controlled by capillary forces, which arise from the combined effects of γ , wettability, and pore geometry. Together, these parameters govern capillary entry pressure, phase distribution, and trapping efficiency, thereby exerting first-order control on injectivity, containment, and cyclic performance.

Capillary pressure represents the pressure required for hydrogen to invade water-filled pores. For an effective pore throat radius, r , capillary pressure (P_c) is described by the Young-Laplace equation

$$P_c = \frac{2\gamma \cos \theta}{r} \quad (5)$$

where θ is the contact angle measured through brine, and r is the effective pore-throat radius. High γ and small r therefore result in strong capillary barriers that restrict hydrogen invasion and promote trapping. Capillary effects manifest differently in storage reservoirs and sealing formations due to their contrasting pore-size distributions. In caprocks characterized by fine pore structures, high capillary entry pressures suppress upward hydrogen migration and constitute the primary containment mechanism for UHS [108]. The equilibrium height, h , of a hydrogen column beneath a sealing unit can be estimated by balancing capillary and buoyancy forces [107]

$$h = \frac{2\gamma \cos \theta}{rg\Delta\rho} \quad (6)$$

Strongly water-wet conditions (smaller $\theta \Rightarrow \uparrow \cos \theta$), and higher IFT ($\uparrow \gamma$) increase h (stronger sealing), enhancing seal integrity, whereas reductions in either parameter weaken capillary containment. Importantly, h is not constant but varies with depth as pressure, temperature, and salinity evolve and modify γ , θ , and $\Delta\rho$ [108]. Within the storage reservoir, capillary pressure regulates horizontal and vertical migration, snap-off frequency, and residual trapping during cyclic injection and withdrawal [41,179]. Fine pore networks impose high capillary thresholds that promote snap-off and the formation of disconnected hydrogen ganglia, whereas piston-like displacement dominates in larger, well-connected pores. The balance between these two processes controls residual gas saturation and recovery efficiency [41,179]. While wettability and IFT modulate fluid-solid interactions, reservoir behaviour is further constrained by pore-throat architecture, expressed through the porosity-permeability relationship. Because porosity and permeability alone do not capture this interplay, integrative metrics have been introduced to bridge pore-scale geometry and multiphase flow behaviour. Among these, the Flow Zone Indicator (FZI), as defined by Eq. (7), has been widely adopted for distinguishing hydraulic flow units and characterizing the efficiency of pore connectivity [27,141]. Typically, rocks with higher FZI indicate more open, efficiently connected pore systems, whereas lower FZI values are characteristic of tighter pore networks that impose stronger capillary entry barriers [27,141].

$$FZI = 0.0314 \frac{1-\phi}{\phi} \sqrt{\frac{k}{\phi}} \quad (7)$$

where FZI is expressed in micrometers, k is permeability, and ϕ is porosity. Experimental capillary pressure-saturation relationships consistently show an inverse dependence between FZI and entry pressure (Fig. 2), linking pore-scale geometry to injectivity and containment performance. Samples characterized by larger FZI in Fig. 2 exhibit lower entry pressures, reflecting the presence of larger and better-connected pore networks. Although high- FZI rocks favour injectivity and deliverability, their reduced capillary resistance limits residual trapping.

Even among samples with comparable FZI , variations in surface chemistry and mineralogy can induce substantial differences in wetting preference and interfacial behaviour [14,54,65,104,128]. Such microscale heterogeneities can reshape capillary pressure curves and displacement pathways. For example, sandstones have been shown to

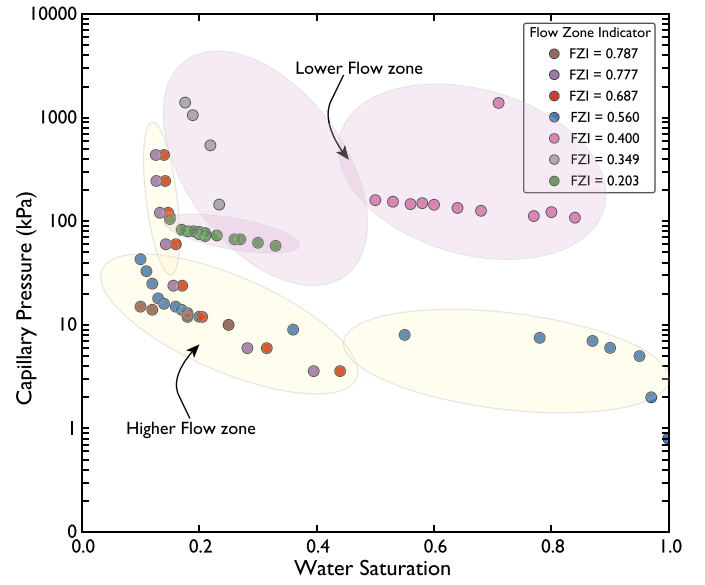


Fig. 2. Capillary pressure-saturation relationships from core-flooding experiments compiled from multiple published studies [41,60,98,132,179,198]. Higher FZI values denote enhanced flow capacity, injectivity, and deliverability, whereas lower FZI values reflect stronger capillary trapping, reduced injectivity, and lower cycling efficiency. The main comparison is therefore the trade-off between pore networks that favour hydrogen mobility and those that provide stronger capillary containment.

undergo wettability transitions when exposed to humic acids, which enhance van der Waals attraction between silica surfaces and hydrogen thereby modifying interfacial interactions [14,65,104,128]. Pore-scale investigations further demonstrate that wettability exerts strong control on displacement behaviour. Using two-phase microfluidic simulations based on the level-set method, Liu et al. [129] systematically explored this dependence across a range of capillary numbers. Under strongly water-wet conditions (contact angles of 20° – 40°), capillary fingering dominated, producing unstable invasion fronts, elevated entry pressures, and frequent snap-off events. These conditions enhanced residual trapping but reduced injectivity. In contrast, at higher contact angles ($\sim 60^\circ$), displacement became more stable, reflecting a transition to viscous fingering that improved injectivity at the expense of trapping efficiency.

IFT (γ) and the resulting wettability are not intrinsic constants. Rather, they are influenced by subsurface conditions, including pressure, temperature, salinity, and the surface chemistry of the rock and fluids [19,66,108,137]. Increasing temperature generally reduces gas-solid interfacial energies (γ_{s-H_2}), promoting hydrogen spreading on mineral surfaces and potentially weakening caprock sealing capacity (Fig. 3, [99,100,149]). A similar trend has been reported for γ_{s-CO_2} systems, attributed to the reduced difference between the cohesive energy density of the gas and that of the rock at elevated pressures [24]. Pressure, while typically influential in gas-liquid systems, has a limited effect on hydrogen-brine γ due to hydrogen's low density and low solubility in brines (Fig. 1c, [5,96]). As shown in Fig. 3, reservoir conditions and surface chemistry strongly influence hydrogen-brine interfacial properties and wettability. Dissolved organic matter (e.g., humic acids) and residual hydrocarbons can adsorb to mineral surfaces, reduce γ , and shift wettability toward intermediate-wet conditions, thereby reshaping film stability, snap-off frequency, and hysteresis [14,104]. For instance, Ali et al. [17] showed that clean quartz, initially strongly water-wet ($\theta_a \approx 40.8^\circ$), became hydrogen-wet ($\theta_a \approx 91.3^\circ$) after ageing in lignoceric acid (10^{-2} M) at 25 MPa and 323 K. It was also reported that pure mica shifted to intermediate-wet at higher pressures and lower temperatures, with organic acids driving it to hydrogen-wet.

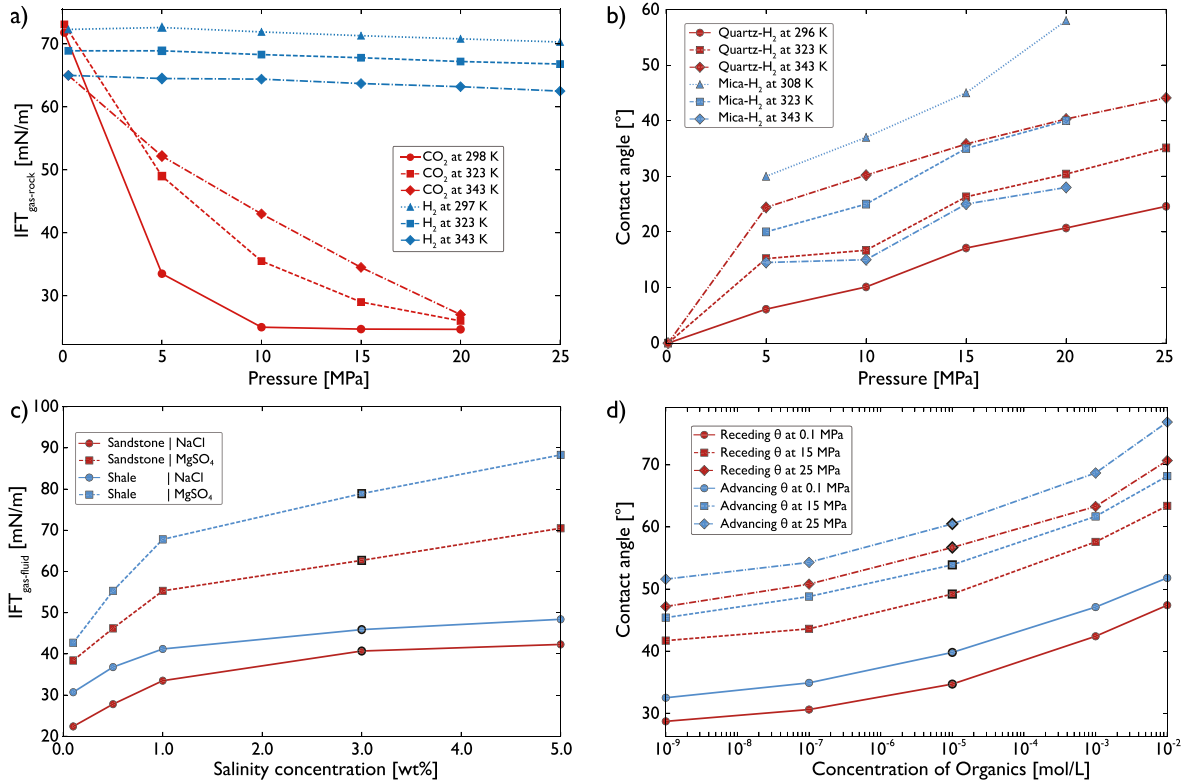


Fig. 3. Effects of reservoir conditions on interfacial properties and contact angles in hydrogen-brine systems. (a) Gas-rock interfacial tension with pressure for hydrogen compared to CO₂ at different temperatures on quartz surfaces, showing temperature-dependent wettability changes. (b) contact angle variation as a function of pressure for hydrogen systems on mica and quartz substrates at various temperatures, demonstrating mineral-specific interfacial behaviour. (c) Effect of salt concentration on gas-fluid interfacial tension for NaCl and MgSO₄ brines in sandstone and shale, highlighting the greater interfacial enhancement from divalent MgSO₄ compared to monovalent NaCl and rock-dependent interfacial properties. (d) Effect of organic matter concentration on advancing and receding contact angles at different pressures, illustrating how organic compounds alter wettability. The panels, adapted from Pan et al. [149], Ali et al. [19], and Iglaier et al. [108], reflect directional sensitivities, with mineralogy, brine composition, pressure, temperature, and organic surface coatings jointly influencing capillary trapping.

Increasing brine salinity typically increases γ and capillary entry pressure (P_{ce}), thereby enhancing containment and capillary sealing (Fig. 3, [5,103]). Mechanistically, Ali et al. [19] showed that increasing salinity compresses the electrical double layer, shifts the zeta potential toward zero (i.e., less negative surface charge), and tends to increase the contact angle, θ . Consistent with this interpretation, Hosseini et al. [99] reported slight increases in θ at higher salinities, implying reduced water-wetness as ion concentration diminishes surface polarity. Pore-scale microfluidic observations by Medina et al. [137] broadly align with this mechanistic framework, showing that higher salinity increases θ (less water-wet) and lowers capillary entry pressure. In addition, salinity raises brine viscosity, thereby increasing the gas-water mobility ratio and modifying front stability and displacement efficiency. However, the salinity response is not universal, as Hashemi et al. [87] observed no statistically significant change in θ across NaCl concentrations of 0, 5000, and 50,000 ppm at 30 °C and 20–100 bar. These results suggest that hydrogen-rock wettability can remain relatively insensitive to salinity under certain mineralogical and thermodynamic conditions. As summarized in Table 1, higher salinity generally increases γ_{H_2-w} and P_{ce} , whereas organic compounds reduce γ and water-wetness, lowering both P_{ce} and residual gas saturation (S_{gr}). Temperature typically decreases γ , while pressure effects remain comparatively minor and mineral-dependent.

Under high gas-brine IFT conditions, structural and residual trapping dominate hydrogen storage behaviour, providing strong capillary containment. In contrast, low-IFT regimes reduce capillary pressure, facilitating hydrogen redistribution within the pore structure and increasing the propensity for gas dissolution and snap-off in water-wet

systems. Elevated salinity therefore tends to create more favourable conditions for UHS by increasing γ_{H_2-w} and P_{ce} , strengthening capillary seals while largely preserving (or slightly improving) water-wet conditions. This combination enhances both structural trapping and residual trapping (higher S_{gr}), yielding a more robust storage system. On the contrary, the presence of organic compounds creates a particularly challenging situation. As shown in Table 1, organic matter drives the system toward less water-wet conditions while simultaneously reducing interfacial tension. This dual effect lowers P_{ce} , weakens structural trapping, and can compromise storage security [19]. Under intermediate-wet or gas-wet conditions, reduced snap-off may improve displacement efficiency and hydrogen mobility by promoting continuous gas pathways. Nevertheless, ultimate recovery can still decline due to weaker pressure support and diminished capillary-driven retention, underscoring the fundamental trade-off between injectivity, mobility, and long-term containment. These coupled interfacial controls define the baseline capillary regime under which hydrogen migration, trapping, and storage security operate.

2.2. Relative permeability, trapping, and cyclic hysteresis

Relative permeability governs the effective mobility of hydrogen and brine during multiphase flow and is a key determinant of injectivity and recoverability in UHS. Experimental studies consistently report low endpoint hydrogen relative permeability (k_{r,H_2}), typically ranging from 0.003 to 0.083, even at moderate gas saturation achieved after primary drainage (Fig. 4, [117,132,158]). This behaviour stems from hydrogen's distinctive physicochemical properties, most critically its high γ with brine, which, together with its low viscosity and density,

Table 1
Directional effects of reservoir changes on interfacial energies and trapping (water-wet baseline, $\theta < 90^\circ$).

Change	γ_{H_2-w} (gas-fluid)	γ_{s-H_2} (gas-solid)	$\cos \theta$ (water-wetness)	Impact (seal P_{ce} , host S_{gr})
Salinity $\uparrow$ (NaCl/CaCl ₂)	$\uparrow$	$\sim$	$\sim$ to $\downarrow$	$P_{ce} \uparrow$ (dominant via γ), $S_{gr} \uparrow$.
Organics / humics $\uparrow$ (e.g., lignoceric, humic acids)	$\downarrow$ to $\sim$	$\downarrow$ (greater spreading)	$\downarrow$ (toward gas-wet)	$P_{ce} \downarrow$, $S_{gr} \downarrow$.
Nanofluid treatment (water-wetting)	$\sim$	$\sim$	$\uparrow$ (more water-wet)	$P_{ce} \uparrow$, $S_{gr} \uparrow$.
Temperature $\uparrow$ (at fixed P)	$\downarrow$ (weak-moderate)	$\downarrow$ (more spreading)	$\downarrow$ to $\sim$ (system-dependent)	Often $P_{ce} \downarrow$, $S_{gr} \downarrow$.
Pressure $\uparrow$ (at fixed T)	$\sim$ (limited for hydrogen-brine)	$\downarrow$ to $\sim$	variable (mineral/chemistry dependent)	Case-specific, with only a small direct effect via γ while wettability may dominate.

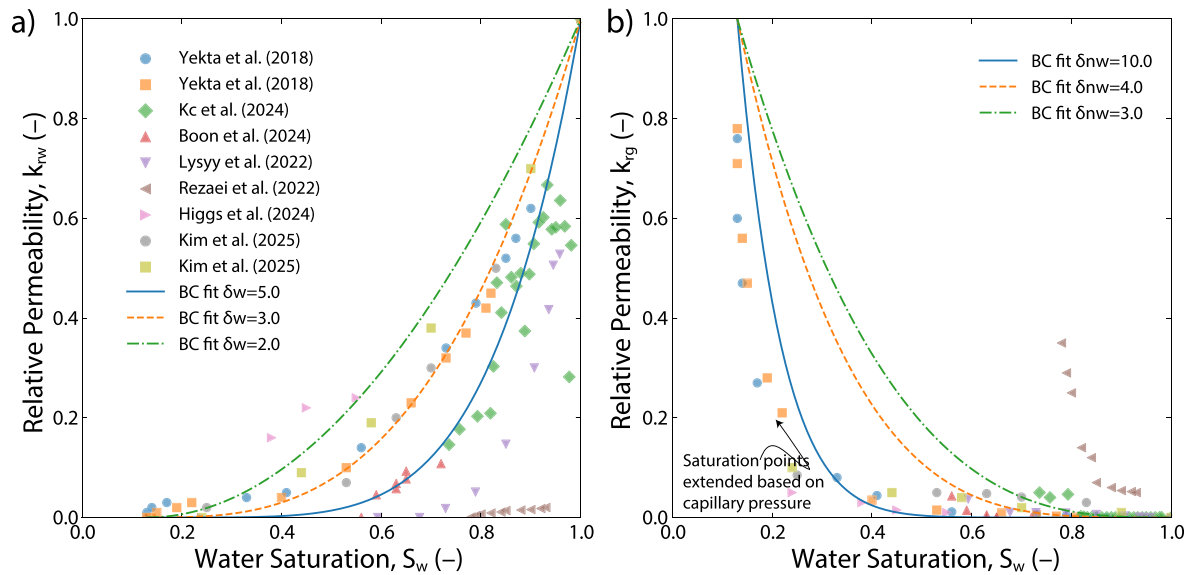


Fig. 4. Relative permeability curves for hydrogen-brine systems, compiled from multiple experimental datasets, compared with Brooks-Corey (BC) empirical fits. (a) water relative permeability (k_{rw}) and (b) gas relative permeability (k_{rg}) as a function of water saturation (S_w), illustrating consistently low end-point hydrogen permeability across datasets, indicative of limited hydrogen mobility during drainage and necessitating higher pressure gradients to sustain injection and storage performance. The spread among datasets reflects differences in pore structure, wettability, flow protocol, and saturation history, so the BC fits are used as comparative descriptors rather than universal constitutive functions.

sets it apart from other gases (Fig. 1c). In contrast, denser and more viscous gases achieve more uniform saturation distributions and improved sweep efficiency [71,158,206], as illustrated in Fig. 5. In most UHS systems, hydrogen behaves as a non-wetting phase, particularly because these systems are strongly water-wetting, and its high γ translates into elevated capillary entry pressures that can restrict invasion into smaller pore throats. This capillary resistance confines hydrogen to larger, better-connected pores, promotes bypassing and disconnected gas clusters, and ultimately reduces the effective cross-sectional area available for connected gas flow. Low viscosity then amplifies this constraint by increasing the gas-brine mobility ratio and favouring unstable displacement or fingering. Consequently, hydrogen mobilizes less efficiently within porous media, often producing unstable displacement fronts and limited pore-space occupancy compared with other gases.

Although this low-mobility behaviour is broadly consistent across studies, a diverging trend was reported by Rezaei et al. [158], who observed comparatively higher end-point k_{r,H_2} values at lower gas saturation. A plausible explanation for this higher k_{r,H_2} is early hydrogen breakthrough through viscous fingering under unsteady-state conditions, which subsequently evolves into preferential flow channels [36]. Once established, these channels dominate flow, producing high apparent core outlet fluxes after breakthrough and artificially elevated k_{r,H_2} estimates, accompanied by reduced water fractional flow. Such channelized flow regimes, widely reported in gas-liquid displacement studies, are characterized by locally high non-wetting phase

saturation but poor overall displacement efficiency [41,173]. During subsequent imbibition, water preferentially bypasses these channels, resulting in minimal residual trapping within them while trapping persists in surrounding regions. This spatial heterogeneity introduces significant uncertainty into relative permeability measurements and complicates direct upscaling of laboratory results to reservoir-scale performance.

The trend shown in Fig. 4 is further contextualized by comparison with conventional gas-brine systems, for which Brooks-Corey parameterizations are more extensively documented [30,33,44,120]. In CO₂-brine flow through Berea sandstone, fitted Corey exponents typically span $n_g \approx 1.6$ –1.8 and $n_w \approx 3.8$ –5.1 [48], with endpoint k_{r,CO_2} values generally falling within 0.06–0.61 across sandstones and reaching ≈ 0.96 in highly permeable Darcy-range samples. Comparable ranges have been reported for carbonate reservoirs [30,33,44]. In contrast, the hydrogen-brine systems shown in Fig. 4 are characterized by substantially lower endpoint k_{r,H_2} values, around an order of magnitude below those reported for CO₂-brine systems on comparable lithologies. The fitted gas-phase Corey exponents span a broader range of $n_g \approx 3$ –10, whereas the water-phase exponents remain within $n_w \approx 2$ –5. The much larger n_g produces markedly steeper $k_{r,g}(S_w)$ curves and a more rapid decline of hydrogen mobility with increasing brine saturation, whereas the water-phase exponents broadly overlap the CO₂-brine range, indicating that wetting-phase mobility is governed more by pore architecture than by the identity of the non-wetting gas. The same offset is reproduced at

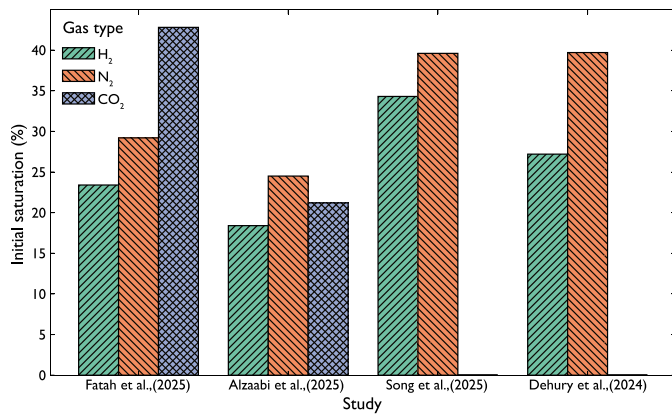


Fig. 5. Initial gas saturation values reported for different gas types (H₂, N₂, and CO₂) across selected studies. Results show that hydrogen generally exhibits lower initial saturations compared to other gases, indicating reduced displacement efficiency which may limit hydrogen storage in porous media. This comparison complements Fig. 4 by showing that reduced hydrogen mobility is commonly accompanied by limited pore-space occupancy during drainage.

the pore scale by microfluidic experiments comparing H₂ with CH₄ and N₂ on identical pore geometries, in which hydrogen consistently attains lower gas saturations at comparable flow rates [71,133], consistent with the higher gas-brine γ and capillary resistance established earlier.

Beyond flow-regime effects, hydrogen relative permeability and trapping are strongly influenced by the wettability and interfacial controls detailed in Section 2.1. Because hydrogen is typically more strongly water-wet than other gases (Fig. 3a), it experiences greater capillary resistance and reduced displacement efficiency. Several studies have demonstrated that shifting the system toward intermediate-wet conditions improves displacement efficiency and gas mobility [61,106]. Accordingly, strategies that reduce γ or modify wettability are expected to improve hydrogen injectivity and pore-space utilization.

Reported values of initial and residual hydrogen saturation span a wide range, reflecting variations in rock petrophysical properties, pore structure heterogeneity, and injection conditions [158,193]. For example, Boon and Hajibeygi [41] measured an initial hydrogen saturation of 47% with a residual saturation of 17%, whereas [8] reported values as low as 4% and 2% under similar Ca (on the order of 10^{-9}). These contrasts underscore the influence of porosity, permeability, and pore connectivity. As illustrated in Fig. 6, residual gas saturation ($S_{g,r}$) generally increases with initial gas saturation ($S_{g,i}$), consistent with Land's trapping model. However, the wide scatter observed across datasets indicates that trapping efficiency cannot be described by saturation alone. Instead, it reflects the underlying pore-scale architecture and flow-unit characteristics noted earlier (Section 2.1). Applying the FZI (Eq. 7) framework reveals systematic trends in which low- FZI samples, representative of tighter and less connected pore systems, cluster near higher trapping-efficiency curves characterized by low Land coefficients (C), whereas high- FZI samples follow lower trapping-efficiency curves with higher C , indicative of enhanced connectivity and reduced residual trapping. These distinctions have direct implications for UHS site selection, as low- FZI flow units may provide greater storage security through enhanced residual trapping but at the cost of reduced deliverability, whereas high- FZI units favour hydrogen recovery but offer weaker long-term immobilization. Balancing these competing attributes of secure containment versus operational flexibility remains a central challenge in evaluating the suitability of candidate storage sites.

Cyclic hysteresis further compounds these effects. Hysteresis arises from the path-dependent evolution of capillary pressure and relative permeability during repeated drainage-imbibition cycles, driven by snap-off, ganglion entrapment, film swelling, flow bypassing, and contact angle hysteresis [32,125]. This behaviour is particularly relevant to UHS,

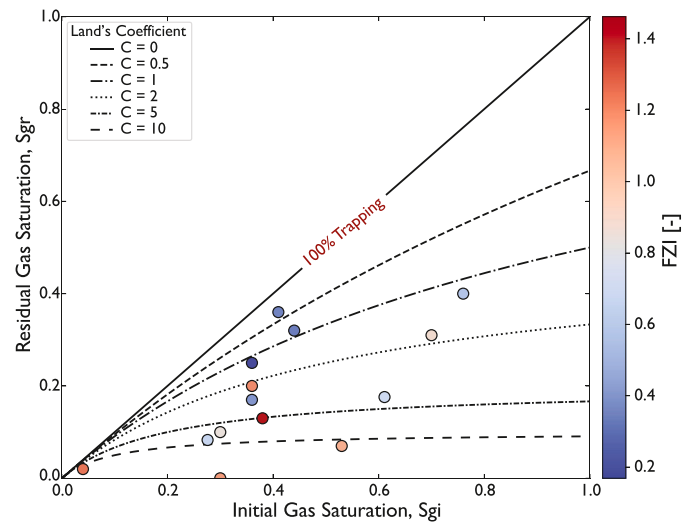


Fig. 6. Relationship between initial gas saturation ($S_{g,i}$) and residual gas saturation ($S_{g,r}$) derived from experimental hydrogen brine core flooding studies (see Tables S4 and S5 for data used in this figure). Data points, colour coded by flow zone indicator (FZI), are compared with theoretical Land's curves for a range of trapping coefficients (C). The plot illustrates the influence of capillary forces and pore structure on hydrogen retention in porous media.

where injection and withdrawal are inherently cyclic and the hydrogen plume geometry and fluid distributions evolve dynamically over time [122]. Steady-state experiments consistently demonstrate pronounced hysteresis between drainage and imbibition for hydrogen-brine systems [41,98,132]. Neglecting hysteresis can therefore lead to systematic overestimation of long-term deliverability, with reported recoverable fractions reduced to 16–25% once hysteresis effects are accounted for [32,66,204].

To better represent UHS operational conditions, several studies have examined multi-cycle hydrogen-brine displacement (Table 2). These investigations reveal contrasting hysteresis behaviour depending on pore structure and flow regime. In relatively uniform pore networks, residual hydrogen saturation often stabilizes after a few cycles, indicating convergence toward a hysteresis equilibrium and limited additional trapping [106,197]. This convergence occurs more rapidly in homogeneous systems, whereas hierarchical or heterogeneous pore networks tend to require additional cycles due to broader hysteresis loops and delayed stabilization. In contrast, other studies report a progressive increase in residual hydrogen saturation across successive cycles without clear convergence, driven by water blocking, ganglion immobilization, and declining pore connectivity [42,76,128]. For example, Gao et al. [76] observed a reduction in porosity utilization from 51.06% to 40.57% over three cycles. Similar trends have been reported at the core scale, where residual gas saturation continues to increase with repeated cycling [42,128]. Additional factors, such as gas dissolution, may also contribute to this buildup and require further investigation to isolate their effects. At larger scales representative of field-scale UHS operations, Lysy et al. [132] observed systematically lower gas relative permeability during imbibition compared with drainage, confirming that hysteresis enhances hydrogen entrapment beyond the pore scale.

Dynamic wettability effects may further reinforce hysteresis. Experimental studies report increases in apparent contact angle between irreducible water ($\theta \approx 44^\circ$) and residual gas saturation ($\theta \approx 57^\circ$), altering capillary pressures and restricting gas mobility [98]. Longer residence times may also promote gas-rock interactions that subtly modify wettability and prolong hysteresis effects. For instance, Herring et al. [95] observed that although the Bentheimer sandstone sample remained predominantly water-wet, subtle indications of a progressive

Table 2

Studies reporting hysteresis behaviour during cyclic hydrogen-brine displacement.

Study & medium	Experimental set-up	Key hysteresis observations
Yang et al. [197]; microfluidic sandstone chip	Cyclic gas-then-water invasion at capillary-dominated flow, ≥ 4 cycles	Both networks approached a “hysteresis equilibrium” after the 3rd-4th cycle the initial/residual saturation trajectories collapsed onto a narrow band. They also observed equilibrium was reached sooner in the uniform network while the hierarchical network needed one extra cycle and exhibited a broader loop, indicating stronger persistent trapping.
Wang et al. [192]; pore-scale simulation (CO ₂ -water)	Interface tracking algorithm, 15 drainage-imbibition cycles were simulated	Hysteresis equilibrium was observed at the 5th cycle where residual saturation remained constant.
Bijay et al. [36]; Berea core	Four charge/discharge cycles at 20 MPa confining stress, sandstone plug	Withdrawal efficiency was $\approx 78\%$ in the first cycle, and increased to $\approx 94\%$ in the second, and remained at that level in cycles 3-4, implying the hysteresis loop stabilized rapidly. Core hydrogen saturation continued to rise slightly, but the amount recovered on each withdrawal reached a steady value.
Ibitogbe and Awolayo [106]; Basalt rock	10 injection/withdrawal cycles, Quasistatic pore network model + micro-CT imaging	Residual saturation increased over the first five cycles before reaching a plateau and stabilizing.

shift toward CO₂-wetting emerged as the experiment progressed. This observation suggests that regions of the solid surface in contact with CO₂ clusters may experience localized wettability alterations, transitioning from initially water-wet to increasingly CO₂-wet as a result of chemical or physical interactions. Nevertheless, most experimental evidence on pristine reservoir rocks indicates that hydrogen does not induce wettability shifts over long-term exposure. Instead, variations in water chemistry, temperature, pressure, and the presence of reactive species are likely to exert stronger controls on wettability evolution [16,107].

These findings show that relative permeability, trapping, and cyclic hysteresis are inseparable components of hydrogen multiphase flow in porous media. Hydrogen's low mobility, strong capillary trapping, and pronounced hysteresis fundamentally constrain injectivity and recoverability, underscoring the need for reservoir-specific characterization and cyclic-performance assessment when evaluating UHS feasibility.

2.3. Post-injection gas redistribution and Ostwald ripening

Following active injection and displacement, hydrogen distribution within porous media does not remain static. Post-injection gas redistribution represents a critical but often underappreciated control on residual trapping, hysteresis, and long-term hydrogen recoverability in UHS systems. While the physical basis of Ostwald ripening (OR) in porous media is well established [38,45,77], its relevance to hydrogen multiphase flow has only recently been examined systematically [59,82,111,206]. Blunt [37] described two end-member post-injection scenarios for multiphase flow in porous media. In the first, gas remains connected across the pore space, forming a classical gravity-capillary transition zone characterized by pressure-driven flow and capillary equilibrium. In the second, water invades previously gas-saturated regions, fragmenting the gas phase into disconnected ganglia. Under this latter condition, advective flow ceases and gas migration proceeds primarily through molecular diffusion in the aqueous phase, a process known as

Ostwald ripening [38,45,77]. Direct pore-scale evidence of this mechanism for hydrogen is shown in Fig. 7, where redistribution of trapped gas occurs during a 12-hour no-flow period.

Ostwald ripening arises from spatial variations in capillary pressure among trapped ganglia, which translate into differences in gas pressure and, consequently, dissolved-gas concentration gradients in the surrounding brine [206]. Although hydrogen exhibits lower aqueous solubility than gases such as CO₂, its substantially higher diffusion coefficient accelerates mass transfer through the aqueous phase. This rapid diffusion promotes gas redistribution between ganglia, causing smaller, high-pressure bubbles to dissolve while larger, low-pressure ganglia grow. Unlike bulk fluids, porous media can sustain multiple ganglia at uniform capillary pressure, allowing OR-driven coarsening without full phase coalescence. In UHS, residual hydrogen trapped at varying capillary pressures is therefore expected to undergo progressive redistribution until local equilibrium is achieved [206]. This process alters ganglia size distributions, connectivity, and effective gas saturation, directly challenging the assumption of static residual trapping following injection.

In addition to OR, pressure-decline-induced gas expansion provides a complementary post-injection mobilization pathway. Unlike injection-driven displacement, which advances primarily along connected pathways under viscous-capillary control, depressurization mobilizes gas throughout the pore space through volumetric expansion and dissolved-phase exsolution [60]. As pore pressure decreases, hydrogen solubility in brine declines, generating aqueous supersaturation that feeds exsolution into nearby ganglia. The resulting increase in local gas pressure relative to capillary entry thresholds ($p_g - p_w \gtrsim P_{ce}$) thins wetting films, depins contact lines, and opens previously subcritical throats. Table 3 summarizes experimental and numerical studies that document OR and gas-expansion effects relevant to UHS. Pore-scale micro-CT experiments by Zhang et al. [206] provided the first direct visualization of hydrogen OR, showing the disappearance of small ganglia and growth of larger ones during quiescent periods (typically 12–16 hours), while N₂ exhibited minimal redistribution under identical conditions. This gas redistribution improves connectivity, lowers local capillary pressure, and reduces residual gas saturation over repeated cycles, thereby narrowing drainage-imbibition hysteresis and enhancing withdrawal efficiency. Similarly, Goodarzi et al. [82] observed that repeated hydrogen injection-imbibition cycles separated by no-flow intervals led to reduced hysteresis, where trapped ganglia underwent a spontaneous Ostwald ripening process driven by the tendency to minimize total free energy. In a study by Dokhon et al. [60] contrasting injection-driven displacement with depressurization-induced gas expansion, pressure decline mobilized hydrogen beyond connected invasion fronts, increased average gas saturation, and reconnected previously isolated clusters. Core-scale imaging by Boon et al. [42] further demonstrated that OR can reshape trapped hydrogen distributions through coupled dissolution near the inlet and exsolution deeper in the core, facilitating partial remobilization of previously trapped gas.

Comparative studies highlight hydrogen's exceptional susceptibility to post-injection redistribution. Several studies have shown that hydrogen undergoes substantially stronger OR-driven rearrangement than N₂ [170,206]. This behaviour was attributed to hydrogen's high diffusivity in water, reaching $5.13 \times 10^{-3} \text{ cm s}^{-2}$, compared with $1.88 \times 10^{-5} \text{ cm s}^{-2}$ for N₂ (Fig. 1c), as well as its small molecular size, which facilitates penetration into finer pore structures [170]. Similar conclusions were drawn by AlZaabi et al. [22], who observed pronounced hydrogen redistribution over laboratory timescales, whereas N₂ and CH₄ remained largely unchanged. Rock heterogeneity further modulates post-injection redistribution by controlling diffusion pathways, ganglia geometry, and equilibration times. Studies by Boon et al. [42] and Lin et al. [126] demonstrate that heterogeneous pore structures with broad pore-throat size distributions can accelerate connectivity gains and amplify OR-driven redistribution, whereas more homogeneous

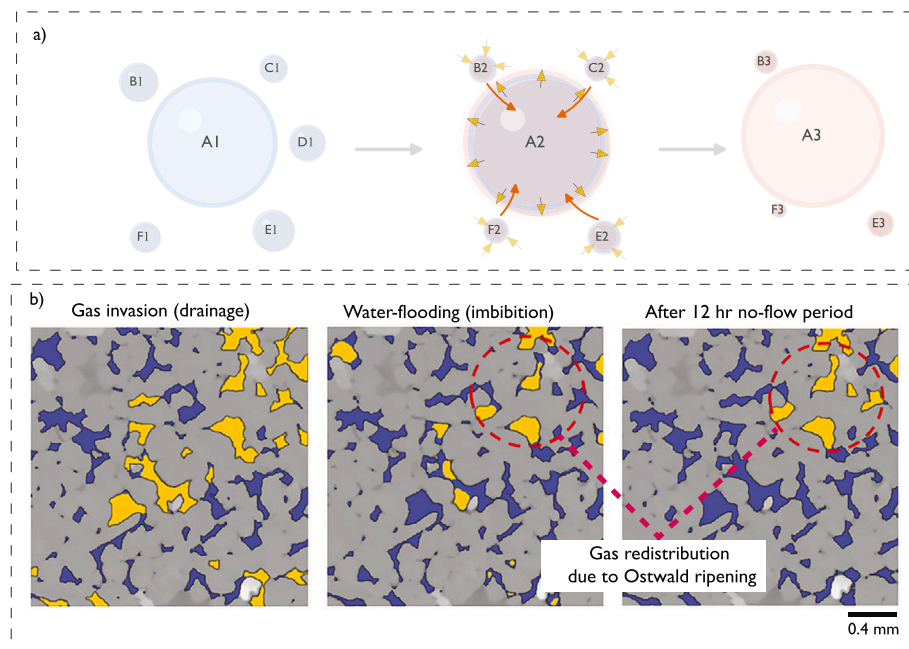


Fig. 7. (a) Conceptual illustration of Ostwald ripening in porous media, where smaller hydrogen ganglia dissolve and transfer mass via molecular diffusion to larger ganglia with lower capillary pressure, resulting in coarsening over time. (b) micro-CT segmented images of Bentheimer sandstone during gas invasion, water-flooding, and after a 12-hour no-flow period. Grey indicates the rock matrix, blue the brine phase, and yellow the hydrogen phase. The highlighted region shows redistribution of hydrogen ganglia, with small bubbles disappearing and larger bubbles growing, consistent with Ostwald ripening dynamics adopted from Zhang et al. [206].

Table 3

Studies highlighting Ostwald ripening and gas-expansion effects relevant to UHS.

Study type	Displacement type	Conditions	Porous medium	Key findings (Ostwald ripening/gas expansion)	Refs
Pore-scale micro-CT	Drainage → imbibition → no-flow (12 h)	~1 MPa, 25 °C	Bentheimer Sandstone	Small hydrogen ganglia disappeared while larger ones grew during quiescence (mass conserved), providing direct pore-scale evidence of OR driven by dissolved-gas concentration gradients, whereas N ₂ showed minimal change.	[206]
Pore-scale micro-CT	Gas injection vs. pressure-decline gas expansion	1 MPa, 20 °C	Bentheimer Sandstone	Pressure-decline expansion increased average gas saturation and helped reconnect otherwise isolated clusters, part of the added volume arose from hydrogen exsolved from brine. Proposed dimensionless metrics to distinguish displacement from expansion.	[60]
Core-scale, multiscale CT	hydrogen injection & imbibition with no-flow holds	–	Berea Sandstone	During no-flow, medium ganglia fragmented while a few larger ones grew consistent with OR-driven redistribution. Dissolution near the inlet and exsolution deeper in the core reshaped disconnected ganglia, culminating in substantial removal of trapped hydrogen.	[42]
Core-scale CO ₂ WAG	WAG cycles, post-flow equilibration	–	Carbonates (contrasting heterogeneity)	Heterogeneity increased the gravity-capillary transition height and shortened equilibration time. Ganglia surface-area/volume scaling ($A \sim V^p$) depended on structure. Dissolved-gas flux induced by concentration gradients can drive CO ₂ redistribution, operating through an OR mechanism.	[126]
Pore-scale micro-CT	Repeated hydrogen injection ↔ brine flooding, 16h no-flow	~1 MPa, 25 °C	Bentheimer Sandstone	OR reduced hysteresis and trapping across cycles. After quiescence, a single large connected ganglion formed with improved connectivity, and capillary pressure and residual gas saturation both declined over cycles.	[82]
Pore-scale micro-CT (comparative)	Separate injections of N ₂ , CO ₂ , hydrogen, brine pre-equilibrated	9 MPa, 60 °C	Carbonates	Hydrogen exhibited stronger post-injection rearrangement and improved connectivity, consistent with OR, whereas N ₂ exhibited minimal change and CO ₂ remained well connected with little rearrangement, which favours hydrogen withdrawal but reduces its effectiveness for long-term CO ₂ trapping.	[22]
Micro-CT imaging	Cyclic hydrogen or N ₂ injection → imbibition → 12 h no-flow	1.5 MPa confining, 0.5 MPa axial, 25 °C	3D-printed sandstone & natural siltstone	Hydrogen underwent OR during no-flow, with bubble coarsening and reduced effective storage/recovery compared to N ₂ , reflecting its higher diffusivity and mobility.	[170]

media tend to preserve residual trapping for longer periods, but at the expense of reduced recoverability.

From a time-scale perspective, Blunt [38] emphasized that laboratory observations of OR often capture systems in partial equilibrium, where OR-driven rearrangement of hydrogen takes place faster than N₂

and CH₄, which require much longer equilibration periods. Their analytical framework estimates pore-scale equilibration times for hydrogen on the order of weeks to months ($t \sim 3 \times 10^6$ s), whereas field-scale equilibration across a 100 m trapped gas column requires timescales on the order of 10^{14} s, approximately eight orders of magnitude longer. This

disparity implies that OR-driven redistribution is unlikely to cause large-scale remobilization of trapped hydrogen over the operational lifetime of UHS projects. Nonetheless, OR remains operationally significant at the pore and near-wellbore scales, particularly in heterogeneous reservoirs and under cyclic pressure conditions, where shorter diffusion paths and frequent pressure cycling can measurably alter ganglia configuration, residual saturation, and hysteresis over just a few operational cycles. These findings demonstrate that post-injection hydrogen trapping is inherently dynamic rather than static. Ostwald ripening and pressure-decline-induced expansion progressively reshape trapped gas distributions, improve connectivity, and reduce hysteresis at small scales, with implications for injectivity, deliverability, and recovery efficiency during cyclic UHS operation.

2.4. Injectivity, deliverability, and cushion gas viability

Injectivity and deliverability impose fundamental operational constraints on UHS, governing the rates at which hydrogen can be injected into and withdrawn from geological reservoirs while maintaining acceptable pressure limits and storage integrity. In porous media systems, injectivity is primarily controlled by intrinsic permeability, effective gas relative permeability, reservoir thickness, and near-wellbore conditions. Deliverability during withdrawal, in turn, depends on pressure support, gas-phase connectivity, and the evolution of gas-water saturation distributions [91,176,209]. Hydrogen's low viscosity and density (Fig. 1c) result in high mobility ratios relative to formation brines, which can enhance apparent injectivity but also promote early gas breakthrough, pressure transients, and reduced sweep efficiency during both injection and production phases [100,119]. As a result, pressure management becomes central to UHS operation, particularly under cyclic injection-withdrawal conditions. Excessive pressure buildup during injection may compromise caprock integrity or induce geomechanical deformation, whereas excessive pressure drawdown during withdrawal can limit deliverability and increase the risk of water production and residual gas trapping [190,209]. These coupled constraints link injectivity and deliverability directly to the requirement for sustained pressure support within the storage reservoir, which is commonly provided by cushion gas.

Hydrogen's displacement behaviour differs fundamentally from that of other injected gases, with direct implications for injectivity, plume stability, and recoverable storage. Displacement experiments by Fatah et al. [71] showed that hydrogen breaks through significantly faster than N_2 and CO_2 under comparable conditions, and microfluidic experiments demonstrated that it attains lower gas saturations than N_2 and CH_4 at low flow rates [133]. These observations are direct consequences of the high mobility ratio and the resulting enhanced fingering and buoyancy-driven instabilities described in Section 2 [97], and have been observed consistently across pore-scale, core-scale, and numerical studies [41,208], underscoring that high injectivity alone does not guarantee efficient sweep or high recoverable capacity. Small-scale heterogeneity further modulates the capillary-viscous balance noted in Section 2.1. In porous systems with broad pore- and throat-size distributions, capillary barriers amplify displacement instabilities, intensifying snap-off and residual trapping during cyclic operation [173]. Pore-scale simulations by Bagheri et al. [31] showed that hydrogen preferentially invades larger pores while bypassing narrower throats with higher capillary entry pressures, allowing greater pore-space occupancy prior to breakthrough, until higher injection rates shift the displacement toward the viscous-dominated regime (Fig. 10).

Experimental investigations of the effect of injection rate have reported contrasting outcomes. While some studies observed improved hydrogen sweep efficiency at higher flow rates, others reported earlier breakthrough and increased front instability [71,193,208]. These apparent inconsistencies largely reflect differences in experimental scale, pore structure, and wettability, as well as whether gas saturation was quantified at breakthrough or after steady state was reached following the

injection of multiple pore volumes (Fig. 8). For instance, Lysy et al. [133] showed that hydrogen achieved lower gas saturation at low injection rates, whereas higher rates produced greater maximum saturations but also generated disconnected gas ganglia that impaired phase connectivity and reduced recovery. In contrast, studies extending injection beyond breakthrough, allowing hydrogen to propagate through connected pathways until steady state was reached, reported increasing pore occupancy with continued injection [127]. This dependence of reported saturation on Ca and measurement protocol is illustrated in Fig. 8 highlighting a methodological gap that complicates direct comparison across studies.

In an effort to reconcile these contrasting outcomes, Wang et al. [193] systematically examined the role of injection strategy on hydrogen flow dynamics. Their results showed that at low injection rates, hydrogen occupied nearly half of the pore space, but with substantial residual trapping upon imbibition. Conversely, high injection rates significantly reduced both initial hydrogen saturation and residual trapping. Importantly, they identified an optimal operational strategy that combined low injection rates with high withdrawal rates, maximizing pore-space occupancy while improving hydrogen recovery efficiency. Complementary pore-scale simulations by Bagheri et al. [31] further demonstrated that intermediate flow rates, corresponding to specific drainage Ca , represent an optimal regime for hydrogen injection and withdrawal. In this regime, displacement efficiency is balanced against the onset of viscous fingering, thereby minimizing hydrogen loss while preserving gas-phase connectivity. At the operational scale, persistent capillary-dominated flow regimes still remain a key obstacle. The combined effect of high gas-brine interfacial tension and the inherently low viscosity of hydrogen limits injectivity under typical subsurface conditions, often necessitating elevated injection pressures to maintain flow. To counter these limitations and stabilize the displacement front, mobility-control methods such as foam or surfactant slugs have been proposed [46]. More recently, blending hydrogen with other gases (e.g., CH_4) has been suggested as an additional strategy, simultaneously lowering γ and increasing effective phase viscosity, thereby improving sweep efficiency and relative permeability [140].

Cushion gas plays a critical role in mitigating these limitations by stabilizing reservoir pressure, maintaining gas-phase connectivity, and preserving deliverability over repeated injection-withdrawal cycles [91]. In porous media storage systems, a substantial fraction of the pore volume is typically allocated to cushion gas, with reported values commonly ranging from 45 to 80%, depending on reservoir properties, pressure limits, economic constraints, and operational strategy [47,79,142,155]. Cushion gas reduces the amplitude of pressure fluctuations and enhances deliverability by preserving connected gas pathways during withdrawal. In its absence, immiscible flow dominates, leading to capillary trapping, fingering, and significant unrecovered volumes, with reported recovery efficiencies as low as 15.5%, compared to up to 89.7% in systems employing cushion gas [80,115].

The choice of cushion gas introduces additional flow and transport considerations, as its density, viscosity, and solubility directly influence pressure support, hydrogen storage dynamics, and recovery [140,162]. For example, heavier cushion gases can enhance the volume of hydrogen injected by occupying a smaller fraction of the pore space, thereby increasing the effective storage volume available for hydrogen [162]. In contrast, lighter cushion gases tend to improve recovery efficiency by reducing density contrasts with hydrogen, which suppresses gravity overriding and viscous fingering during injection and withdrawal. Using hydrogen as its own cushion gas avoids compositional contamination but increases the amount of unrecoverable working gas and may amplify losses associated with dissolution or microbial consumption over long storage periods [4,7]. Alternatively, inert or weakly reactive gases (Table 4), such as nitrogen (N_2), have been proposed as cushion gas to reduce hydrogen losses and improve working gas efficiency, although gas-gas mixing, differential mobility, and separation during withdrawal introduce further operational complexity [155,176]. For example, the

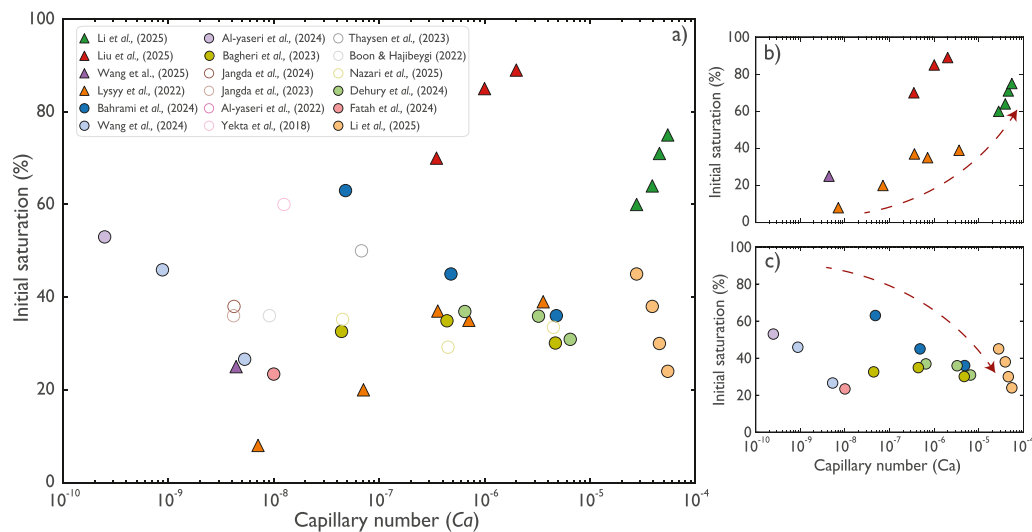


Fig. 8. Impact of capillary number on hydrogen phase distribution during drainage, based on studies compiled in this work [31,32,41,55,126,130,145,179,195,198]. References for the additional datasets included in the plot are provided in the supplementary material (Table S5). Open circles represent studies that did not specify whether saturation was measured at breakthrough or after stabilization, triangles denote steady-state measurements, and filled circles indicate breakthrough measurements. Although the open-circle data generally follow the trend of decreasing initial saturation with increasing Ca , the lack of measurement timing information introduces a methodological gap that limits comparability across studies.

use of CO_2 as a cushion gas has been shown to increase the purity of produced hydrogen but may also induce density-driven downward convection, thereby favouring hydrogen dissolution into the aqueous phase [207]. Conversely, CH_4 and N_2 as cushion gases enhance hydrogen production rates and mobility [1], but may pose different challenges related to pressure and temperature constraints. Cushion gas selection is further complicated by interactions with in-situ biogeochemical conditions, including microbial activity, residual hydrocarbons, and formation brines. These trade-offs highlight that cushion gas selection is not merely a design choice but a coupled flow-control problem that directly influences injectivity, deliverability, and effective storage capacity.

Storage capacity in UHS is therefore not an intrinsic property of the porous media, but an emergent outcome of coupled multiphase flow processes. Effective working gas capacity depends on the partitioning of pore space between cushion gas, mobile hydrogen, and residual gas trapped by capillary forces, as well as on the evolution of relative permeability and hysteresis during cyclic operation [85,100]. High injectivity does not necessarily translate into high recoverable capacity if buoyancy-driven segregation, capillary trapping, or gas-water hysteresis limit hydrogen recovery during withdrawal. Conversely, conservative pressure management and larger cushion gas volumes may enhance deliverability but reduce the fraction of hydrogen that can be economically recovered. Importantly, most existing experimental and numerical studies treat injectivity, deliverability, cushion gas requirements, and storage capacity in isolation, often neglecting their coupled evolution during repeated injection-withdrawal cycles. This limitation underscores the need to interpret reported storage capacities and performance metrics within the context of the underlying flow assumptions. In practice, injectivity limits, pressure constraints, cushion gas allocation, and working gas recovery are inseparable components of a single multiphase flow system whose behaviour is strongly conditioned by hydrogen's unique transport properties and by reservoir heterogeneity.

2.5. Experimental characterization of hydrogen-fluid-rock systems

Mechanistic understanding of UHS performance relies on integrated experimental and numerical evidence spanning pore to core scales. Because hydrogen flow in porous media is governed by pore-scale physics yet manifests operational consequences at the reservoir scale, no

single method is sufficient to fully characterize its behaviour. Instead, insight emerges from the integration of complementary experimental and modelling approaches, each with distinct strengths and limitations.

2.5.1. Coreflooding protocols and macroscopic flow functions

Coreflooding remains the benchmark laboratory approach for measuring hydrogen-brine multiphase flow properties in reservoir rocks [118,153]. In a typical workflow (Fig. 9), cylindrical core plugs representative of the target formation are confined under reservoir-relevant pressure, temperature, and stress while hydrogen and brine are injected and extracted under controlled boundary conditions [177,198]. Monitoring differential pressure and produced-phase composition enables estimation of key constitutive relationships, including relative permeability, capillary pressure, residual saturation, and wettability effects [96,158,179,198]. Two main experimental protocols are commonly applied as presented in Fig. 9a and b. Steady-state co-injection fixes fractional flow and allows saturation to equilibrate at each condition, supporting high-fidelity relative permeability measurements and, where feasible, direct capillary pressure determination from phase pressure differentials [94]. However, steady-state protocols can be time-intensive at low Ca and may be affected by boundary complications such as phase separation and end effects [36]. Transient (unsteady-state) displacement, by contrast, injects one phase (e.g., hydrogen) continuously into a core pre-saturated with the other (e.g., brine) until breakthrough, with flow functions inferred from pressure and effluent histories using inverse analytical methods (such as Johnson-Bossler-Naumann analysis) or numerical history matching [29,153]. Although faster and less fluid-demanding, unsteady-state methods are generally more sensitive to capillary end effects and boundary-condition uncertainties [28]. This sensitivity reinforces the need for carefully designed experimental workflows, matched to the objective of the study, to reliably characterize hydrogen-brine interactions under storage conditions [23].

Despite their central role, coreflooding measurements are bulk averages that cannot uniquely resolve the pore-scale mechanisms responsible for the observed macroscopic response [153,177,198]. Processes such as snap-off, ganglion mobilization, and preferential pathway development are not directly observable from pressure and effluent data alone [111,112]. This limitation has driven the integration of advanced imaging with flooding experiments (Fig. 9c), enabling direct visualization of hydrogen and brine phase distributions and their evolution during

Table 4
Comparison of key factors influencing the suitability of candidate cushion gases for UHS [1,155,162].

Variable	CO ₂	N ₂	CH ₄
Gas Properties	Dense, high viscosity, corrosive, and reactive under certain conditions.	Inert, non-corrosive, and low density.	High energy content, flammable, and compatible with existing gas infrastructure.
Availability of Cushion Gas	Widely available as a by-product of industrial processes.	Abundant in the atmosphere, but separation and purification are costly.	Widely available, produced from natural gas reservoirs.
Advantages	Cost-effective, with high density enabling better pressure support and good injectivity.	Non-corrosive and chemically inert, and easily manageable.	High recovery potential, compatible with existing systems.
Limitations	Corrosive under certain conditions, with potential for carbonic acid formation.	Requires higher volumes due to low density, and less effective at maintaining high pressure.	Safety risks due to flammability, and higher cost compared to CO ₂ and N ₂ .
Long-Term Stability Effects	Can react with water to form carbonic acid, leading to corrosion.	Chemically stable and inert over time, and favours capillary sealing due to water-wet conditions.	Stable and effective at pressure maintenance, but poses long-term safety concerns.
Wettability and IFT Impact	May shift rock wettability from water-wet to mixed-wet, with higher interfacial tension.	Limited data, with likely minimal impact on wettability.	Alters wettability toward gas-wet, supporting good phase separation due to high IFT.

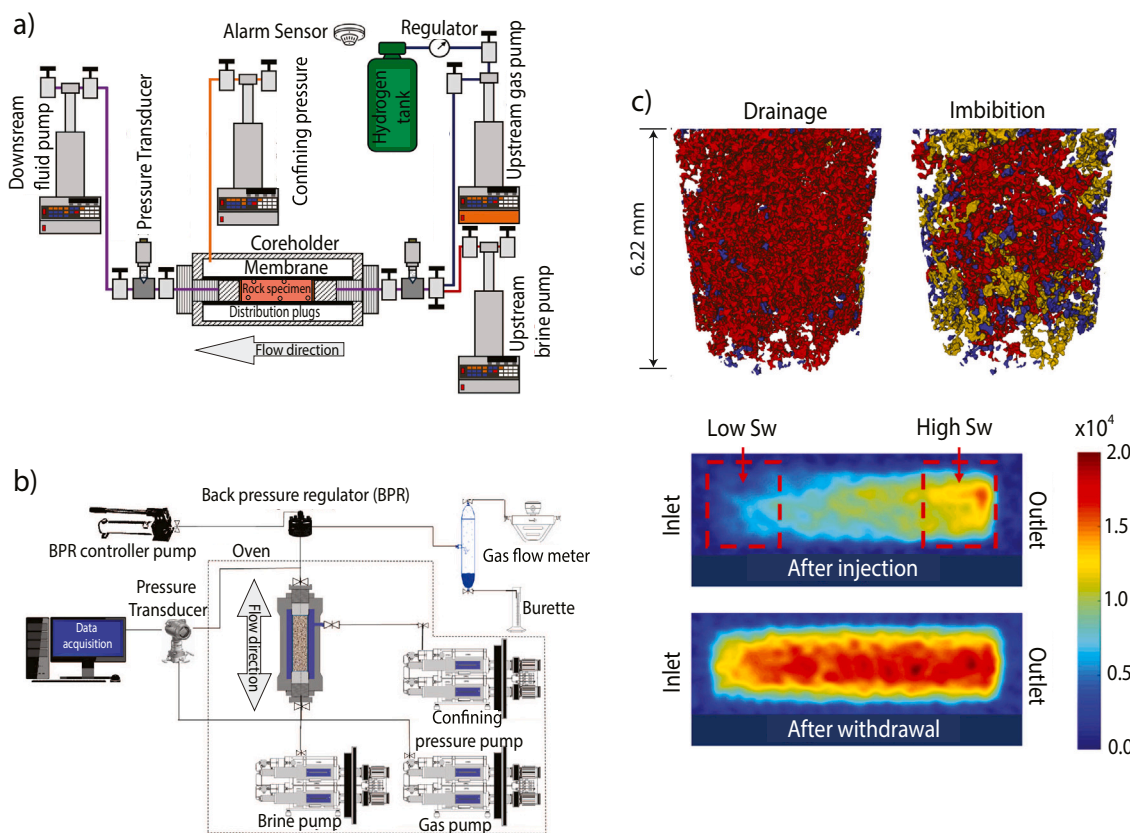


Fig. 9. Coreflooding experimental setups used to provide insights into hydrogen-brine multiphase flow behaviour. (a) the steady-state method establishes equilibrium by co-injecting hydrogen and brine at fixed fractional flow rates, albeit with longer experimental durations, adapted from Kim et al. [117]. (b) the unsteady-state method involves dynamic displacement of hydrogen into initially brine-saturated cores, allowing faster experiments and characterization of breakthrough and transient flow behaviour, adapted from Mirchi et al. [140]. (c) Three-dimensional micro-CT renderings of the hydrogen phase in a sandstone core plug, showing the initial gas distribution following primary drainage and the residual gas distribution after brine imbibition. Gas ganglia are coloured by volume relative to a representative pore size, $\bar{S} = 1.12 \times 10^6 \mu\text{m}^3$, with red denoting volumes greater than $100\bar{S}$, yellow denoting $10\text{--}100\bar{S}$, and blue denoting less than $10\bar{S}$, adapted from Jangda et al. [111]. Bottom panel shows NMR T_2 (transverse relaxation time) spatial imaging of fluid-filled pores following cyclic H₂-water coreflooding experiments, adapted from Wang et al. [194].

displacement [82,206]. High-resolution micro-computed tomography (micro-CT) imaging is now routinely used to link core-scale flow functions to pore-resolved configurations, including the morphology and connectivity of trapped gas, and to capture dynamic displacement behaviour where temporal resolution is available [168,178]. Primarily, static (3D) post-flood scans and dynamic (4D) time-resolved scans have

been employed, depending on whether the objective is equilibrium saturation structure or transient displacement dynamics [42,112,178].

A key technological limitation of micro-CT for hydrogen-brine systems is hydrogen's very low X-ray attenuation, which produces poor phase contrast against brine and routinely necessitates dopants in the brine (for example potassium iodide), dual-energy acquisition, or

substitution with higher-attenuation surrogate gases, each of which can perturb the interfacial chemistry being studied [111,112,177]. The intrinsic spatial-versus-temporal resolution trade-off further constrains direct observation of fast displacement events such as Haines jumps, which unfold on millisecond timescales that lie at the edge of laboratory micro-CT and even synchrotron-tomography capability [172,178]. Complementary core-scale imaging using nuclear magnetic resonance (NMR) provides spatially resolved hydrogen-brine distributions and saturation changes during cyclic injection-withdrawal, supporting interpretation of trapping and redistribution that may not be apparent from bulk metrics [124,193,194].

Building on these methodological foundations, a growing body of core-scale and pore-scale studies has begun to elucidate how hydrogen-brine multiphase flow responds to reservoir conditions, rock properties, and operational history. In one of the earliest systematic investigations, Yekta et al. [199] conducted steady-state hydrogen-water coreflooding experiments on Vosges sandstone and reported nearly identical relative permeability (k_r – S_w) relationships across a range of pressures and temperatures. This invariance was attributed to hydrogen's weak sensitivity of viscosity to thermodynamic conditions, highlighting a degree of robustness in hydrogen flow behaviour under steady conditions. In contrast, subsequent studies, particularly those employing transient flooding protocols, have revealed substantially greater variability in hydrogen transport behaviour. Rezaei et al. [158] investigated hydrogen-brine displacement across multiple lithologies and demonstrated pronounced sensitivity of k_r to rock heterogeneity and brine salinity, highlighting the importance of petrophysical variability in controlling hydrogen mobility under more dynamically representative conditions. Extending these observations to cyclic operation, Lysy et al. [132] examined repeated drainage-imbibition sequences in sandstone formations and showed that trapped hydrogen plays a critical role in shaping relative permeability hysteresis and withdrawal behaviour, with residual gas accumulation progressively reducing effective mobility during withdrawal.

Direct pore-scale observations have provided further insight into the mechanisms underlying these macroscopic responses. Using high-resolution micro-CT imaging during coreflooding, Jha et al. [112] observed substantial residual hydrogen trapping (up to 41%) in Gosford sandstone following hydrogen displacement and brine imbibition. Their results showed preferential re-occupation of smaller pores and pore throats by brine, consistent with strongly water-wet conditions and capillary-dominated trapping. Beyond quantifying trapped phase distribution, several studies have also identified systematic spatial variations in phase distribution along the core length. For example, Higgs et al. [97] demonstrated that when injection pressure was not maintained, water imbibed preferentially near the outlet, generating axial saturation gradients. Similarly, Goodarzi et al. [82] observed higher hydrogen saturation near the inlet and lower saturation toward the outlet following primary drainage. Such gradients can arise from a combination of strong water wettability, outlet boundary effects, and capillary end effects associated with discontinuities in the pressure gradient along the sample.

Following these foundational experiments, a number of investigations have systematically explored the influence of pressure, temperature, injection rate, and rock properties using both steady-state and transient coreflooding approaches. Table S4 synthesizes key laboratory studies across a range of lithologies and conditions, illustrating how variations in petrophysical heterogeneity, wettability, and Ca translate into distinct flow responses and trapping behaviour. Laboratory-scale experiments are typically designed to replicate anticipated field-scale injection protocols, with injection rates deliberately kept low to reflect realistic reservoir operations, minimize geomechanical disturbance, and limit excessive near-wellbore pressure buildup [117]. Analysis of compiled experimental data across published hydrogen-brine coreflooding studies further confirms that these laboratory investigations operate within capillary-dominated flow regimes. As illustrated in Fig. 10, reported experiments cluster at extremely low Ca ($\sim 10^{-9}$ – 10^{-6}), where

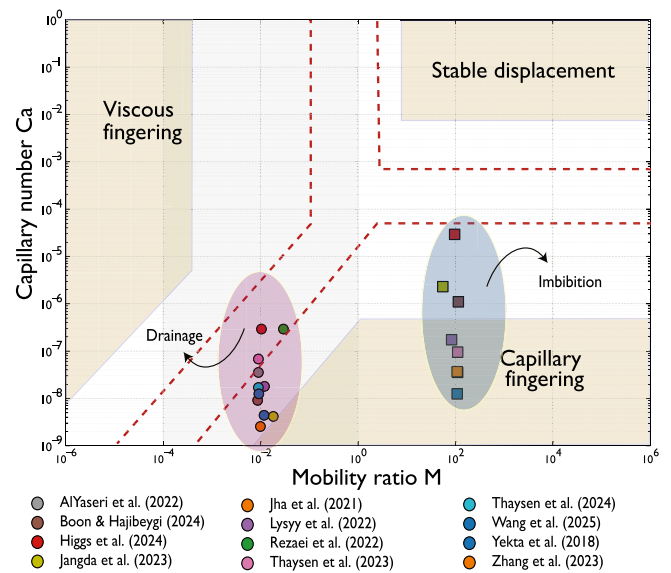


Fig. 10. Phase diagram illustrating displacement regimes in hydrogen-brine systems as a function of capillary number (Ca) and mobility ratio (M) during drainage and imbibition. The regimes are delineated using experimental coreflooding data compiled from recent studies (cf. Table S4), highlighting the coupled influence of viscous and capillary forces on displacement behaviour under reservoir-relevant conditions.

capillary forces strongly outweigh viscous forces regardless of displacement direction. During drainage, data points occupy a relatively narrow mobility-ratio range ($M \sim 10^{-2}$ – 10^{-1}), consistent with capillary-controlled hydrogen invasion and limited sweep efficiency. During imbibition, experiments shift toward substantially higher mobility ratios ($M \sim 10^1$ – 10^2) while remaining at similarly low Ca , placing hydrogen recovery firmly within the capillary-fingering regime. This systematic separation between drainage and imbibition highlights the asymmetric nature of hydrogen displacement under cyclic injection-withdrawal, where capillary trapping dominates withdrawal behaviour and viscous stabilization is rarely achieved under reservoir-relevant injection rates.

These observations underscore a key limitation of macroscopic flow functions derived from laboratory experiments. Relative permeability and capillary pressure relationships measured under capillary-dominated conditions may not extrapolate straightforwardly to scenarios where higher injection rates or altered pressure management shift the balance toward viscous or gravity-controlled flow. As such, interpretation of coreflood-derived parameters must be explicitly conditioned on the displacement regime in which they were obtained, reinforcing the need to integrate macroscopic measurements with pore-scale visualization and numerical upscaling to achieve predictive relevance for UHS operations.

2.5.2. Microfluidics for pore-scale investigation and visualization

Microfluidic micromodels (Fig S1) provide a complementary pathway to pore-scale insight by enabling real-time pore-resolved visualization of hydrogen-brine displacement, including flow instabilities, capillary trapping, and ganglia formation [130,134]. These observations provide quantitative insight into phase connectivity, saturation evolution, and the multiphase interactions that govern hydrogen migration and trapping in porous media [128,169]. Although scaling to field conditions and the representativeness of mineralogical heterogeneity remain recognized limitations, microfluidics offer unique advantages through direct optical access, rapid pore-scale dynamics experimentation, and controllable pore geometry [127,130,131,169]. Rock-patterned micromodels and engineered networks can reproduce key aspects of porous structure while allowing systematic investigation of operating pressure, injection

Table 5

Summary of microfluidic and pore-scale experimental studies investigating hydrogen-brine multiphase flow behaviour under reservoir-relevant conditions.

Micromodel / Device	Conditions	Ca	Key findings	Refs
Silicon wafer etched from sandstone	20 °C, 0.5 MPa	–	Identified preferential, floating, and dead-end flow, higher flux promoted floating/dead-end invasion.	[169]
DRIE-etched silicon (sandstone pattern)	20 °C, 0.5 MPa, DI water	7.68×10^{-7} – 3.84×10^{-4}	Hydrogen saturation rose with Ca , observed I_1/I_2 imbibition and contact-angle hysteresis (17°–56°).	[130]
Etched glass sandstone model	25 °C, synthetic brine with salinity of 96.55 g/L	–	Cyclic injection increased residual hydrogen via ganglion entrapment, large pores retained water.	[76]
DRIE-etched silicon (sandstone-like)	Room pressure, DI water	6.8×10^{-7} – 7.7×10^{-5}	Residual saturation stabilized at 30–40%, some ganglia reconnected in larger pores.	[134]
Heterogeneous pore model and CFD	50–70 °C, 15–25 MPa	–	Viscous fingering observed, storage efficiency 46% lower than N_2 at 50 °C, improved at 70 °C.	[55]
Glass chip ($\phi = 0.33$)	56 °C, 5.6 MPa (Injection), 6.6 MPa (Confining)	2.77×10^{-5} – 5.47×10^{-5}	Displacement showed fingering, gas blocking, and equilibrium, higher injection improved storage, gravity aided migration but increased water trapping.	[127]
3D-printed hierarchical vs. uniform	25 °C, 0.1 MPa, N_2 -water cycles	–	Hierarchical media showed weaker hysteresis but lower recovery due to limited ganglia mobilization.	[197]

rate, and number of injection-withdrawal cycles that control hydrogen residual trapping and recovery [21,133,137,197]. In UHS studies, these platforms have been used to isolate how Ca and wettability-dependent interface dynamics govern phase connectivity and trapping pathways during injection and withdrawal, thereby providing mechanistic context for trends inferred from core-flooding data [130,134,197].

Using etched silicon wafers, glass micromodels, and increasingly 3D-printed porous architectures, recent studies have systematically tracked the evolution of non-wetting phase configurations during injection and withdrawal cycles under well-controlled geometrical and flow boundary conditions [76,131,169,197]. Key experimental conditions and outcomes from these investigations are summarized in Table 5. Across this body of work, a consistent set of pore-scale displacement mechanisms emerges, including snap-off, piston-like advancement, preferential pathway flow, floating flow, and film swelling, influencing hydrogen storage efficiency and withdrawal dynamics [130,169]. Despite variations in micromodel design and operating conditions, capillary-driven trapping consistently dominates hydrogen immobilization, whereas wettability and pore structure primarily control the magnitude and spatial distribution of residual saturation [83]. Viscous and gravitational forces become influential only under specific regimes, including elevated capillary numbers or strong density contrasts [127].

Microfluidic studies further reveal that capillary trapping is strongly conditioned by pore-throat geometry, coordination number, and fluid properties. For example, Lysy et al. [130] identified an I_1 imbibition mechanism in which hydrogen initially occupying multiple adjacent pores was redirected into a single pore due to interfacial instabilities and detachment from pore walls, thereby enhancing local displacement efficiency. At low Ca , piston-like displacement was also observed, characterized by stable advancement of the displacement front through individual pore channels constrained by narrow throats and neighbouring geometries. Complementary observations by Guo et al. [83] documented a floating-flow phenomenon in which buoyancy induces vertical stratification between hydrogen and formation brine, with hydrogen forming a distinct, continuous layer above the aqueous phase. In contrast, Yang et al. [197] showed that hierarchical (dual-permeability) media exhibit weaker hysteresis than uniform pore structures, yet paradoxically yield lower hydrogen recovery due to enhanced second-order trapping within smaller, less accessible pore regions.

Displacement efficiency and residual trapping are further modulated by Ca and wettability, with higher injection rates (larger Ca) promoting hydrogen mobilization during imbibition [130,169]. This rate sensitivity is compounded by contact-angle hysteresis, which induces non-unique, nonlinear saturation pathways. Lysy et al. [130] reported dynamic contact angles spanning 17°–56°, indicating strong history dependence in

phase occupancy. As a result, ganglion mobilization and trapping reflect prior drainage-imbibition sequences, a behaviour that mirrors trends inferred from core-scale experiments and provides a mechanistic basis for understanding how repeated cycling progressively alters relative permeability and effective storage capacity. The dominant pore-scale mechanisms governing hydrogen displacement, trapping, and dissolution are synthesized in Table 6, with their implications for storage security and recovery.

Overall, microfluidic studies show that hydrogen storage behaviour does not follow a single displacement mode, but instead reflects the superposition of multiple capillary-controlled processes whose relative importance varies with Ca , wettability, pore architecture, and flow history. These observations provide the framework needed to interpret core-scale flow functions and highlight the necessity of explicitly representing trapping and hysteresis when extrapolating laboratory observations to the reservoir-scale.

2.5.3. Interfacial measurements and capillary-pressure determination

Because multiphase hydrogen flow is controlled largely by IFT and wettability (Section 2.1), dedicated measurements of contact angle, θ , and IFT, γ , provide essential supporting constraints for characterizing displacement behaviour, fluid distribution, and trapping efficiency [80,106,163]. A variety of optical methods are routinely employed to measure θ under reservoir-relevant pressure, temperature, and brine chemistry, with specialized high-pressure, high-temperature (HPHT) optical cells used for HPHT in-situ reservoir conditions. In the sessile-drop method, a droplet of brine or gas is placed on a flat mineral or rock substrate, and the static contact angle at the three-phase contact line is determined from high-resolution images [5,52]. In the captive-bubble method, a gas bubble is introduced beneath a brine-submerged solid surface, where buoyancy pins the bubble to the underside of the sample and allows wettability to be inferred from its equilibrium shape [86,139]. The tilted-plate method incrementally inclines the substrate to measure advancing and receding contact angles as droplets move, providing a direct measure of contact angle hysteresis associated with surface roughness and heterogeneity [25,108]. In addition, microfluidic visualization in pore-scale micromodels enables in-situ estimation of contact angles by resolving interface curvature during dynamic displacement, providing complementary information under flowing conditions that more closely resemble subsurface hydrogen injection and withdrawal [160].

Hydrogen-brine IFT has been quantified using the same established experimental techniques, often paired with wettability characterization, including pendant-drop, spinning-drop, and captive-bubble methods, which allow measurements under reservoir-relevant conditions [50, 135]. The sessile-drop method estimates IFT from the geometry of a

Table 6

Pore-scale mechanisms governing hydrogen displacement, trapping, and dissolution, with experimental conditions and implications for storage security.

Mechanism	Conditions	Process description	Storage & trapping significance
Preferential-to-uniform flow	Low/high N_{Ca} , pore throat size	Hydrogen first moves through preferential paths (inertia-, capillary-, or oil-blocked flow) before spreading more uniformly.	Uniform displacement improves pore space use and storage efficiency.
Floating flow	Moderate-high Ca , buoyancy	Hydrogen rises above brine/oil, forming overlapping layers due to density differences.	Opens extra pore space but makes saturation harder to measure.
Dead-end pore invasion	Variable, aided by floating flow	Hydrogen enters wall-bounded or converging dead-end pores.	Adds to long-term trapping and storage security.
Reconnection of H_2 ganglia	Cyclic injection-withdrawal	Residual clusters reconnect with new hydrogen during later cycles.	Explains hysteresis, lowers efficiency and capacity over cycles.
Roof snap-off	High Ca , water present	Hydrogen disconnects at throats when the non-wetting phase destabilizes after entering a pore.	Forms isolated clusters that may stay trapped.
I_1 imbibition displacement	Low Ca , narrow throats	Hydrogen is displaced piston-like as brine enters through single channels.	Controls early imbibition, orderly but limited storage.
I_2 imbibition displacement	Medium-high Ca , high coordination number	Brine bypasses and disconnects large hydrogen clusters via narrow throats.	Main cause of residual trapping, reduces recovery.
Film swelling	Post-drainage water injection	Water films expand at pore walls, lowering capillary pressure and splitting hydrogen into clusters.	Promotes capillary trapping and residual saturation.
Dissolution	Prolonged water injection, Ca -dependent	Hydrogen dissolves at one end, both ends, or via mobilized bubbles.	Leads to hydrogen loss, rate set by water front velocity.

Table 7

Summary of experimentally measured interfacial tension for hydrogen-brine systems under reservoir-relevant conditions.

Fluids	T (°C)	P (MPa)	Method	IFT (mN m ⁻¹)	Refs
H_2 & brine (NaCl 48.75%, KCl 31.49%, $MgCl_2$ 12.64%, $CaCl_2$ 7.12%)	20–80	1–10	Captive drop	24–82	[67]
H_2/H_2-CH_4 & brine (0–3.42 M NaCl)	22–60	6.9	Rising/captive bubble	53.55–70.36	[140]
H_2-CO_2 & synthetic brine (NaCl & KCl at 1.05 M and 3.15 M)	50–80	3.4–20.7	Pendant drop	32.1–67.8	[109]
H_2 & 1.05 M synthetic brine (NaCl & KCl)	25–150	2.7–34.5	Pendant drop	46.97–80.77	[100]
H_2 & brine (0–85.6 mM NaCl)	25	6.9–20.7	Captive bubble and pendant drop	56.5–72.45	[96]

droplet resting on a solid surface immersed in another fluid [52,154]. More recently, refinements to these methods such as axisymmetric drop shape analysis have been introduced to improve accuracy by fitting high-resolution droplet profiles to theoretical shapes, enabling robust IFT determination under dynamic and non-equilibrium conditions [123,143]. Practically, only the fluid-fluid IFT is measured directly because the solid phase is immobile at the interface [101,116]. Solid-fluid interfacial energies (γ_{s-H_2} and $\gamma_{s-brine}$) are therefore inferred indirectly using thermodynamic models, such as the reformed Neumann equation of state [146], whereby measured contact angles or independently determined $\gamma_{H_2-brine}$ are combined to satisfy Young's equation (Eq. 4). Reported hydrogen-brine IFT values as summarized in Table 7 span a wide range and exhibit systematic dependence on salinity, temperature, pressure, gas composition, and experimental methodology. This variability is critical because IFT not only dictates hydrogen injectivity but also couples directly with wettability to control capillary entry pressures, residual trapping, and long-term containment behaviour in porous reservoirs [4,106]. A detailed synthesis of IFT and wettability measurement methodologies, together with their implications for UHS, is provided by Aslannezhad et al. [26].

Capillary pressure governs both the entry pressure required for hydrogen to invade water-filled pores during drainage and the extent of residual trapping that develops during subsequent brine imbibition. This dual role is central to hydrogen plume stabilization, trapping efficiency, and cyclic storage performance [106,112,140]. Experimental approaches for determining capillary pressure span a wide range of length scales and methodologies. Direct techniques include porous-plate measurements [82,198,203], high-speed centrifuge methods [158,179], and mercury intrusion porosimetry [41,158]. Indirect estimates are commonly derived from coreflooding experiments as discussed above through pressure-drop analysis, inverse modelling or history matching, or from image-based curvature analysis [81]. In hydrogen-brine systems, microfluidic platforms and dynamic micro-CT have become indispensable for resolving real-time interface evolution and capillary-controlled displacement at the pore scale with high temporal fidelity. By contrast, coreflood-based methods provide bulk-averaged capillary pressure behaviour representative of larger volumes, but remain sensitive to capillary end effects, boundary conditions, and saturation gradients, as discussed earlier. Together, these complementary approaches provide the experimental basis for constraining capillary pressure behaviour across scales relevant to UHS.

Overall, the current evidence base for hydrogen multiphase flow is built on the complementarity of bulk core-flooding measurements, pore-scale imaging and microfluidics, and interfacial and capillary-pressure characterization. This integration is essential for establishing robust flow functions, resolving the mechanisms that govern trapping and hysteresis, and enabling robust upscaling from laboratory observations to reservoir-scale storage and recovery forecasts [74,82].

3. Bio-geochemical controls on hydrogen flow dynamics

The multiphase flow controls described above are commonly interpreted using a fixed set of pore scale and interfacial properties, including wettability, interfacial tension, capillary entry pressure, and relative permeability. During UHS, these properties can evolve as hydrogen interacts with formation brines, mineral surfaces, and resident microbial communities. As a result, bio-geochemical processes do not operate independently of multiphase flow, but instead act as time-dependent feedback that can progressively modify the same controlling variables that govern displacement, trapping, hysteresis, and cyclic recovery. They can also affect operational metrics, including injectivity, deliverability, and recovered gas quality.

Table 8
Possible geochemical and biochemical pathways during UHS.

Process	Microorganism or driver	Reaction	Impact on UHS
Biochemical	Methanogenesis (<i>hydrogenotrophic methanogens</i>)	$4\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	Converts stored H_2 to CH_4 , reduces retrievable hydrogen, alters gas composition and calorific value.
	Acetogenesis (<i>acetogens</i>)	$4\text{H}_2 + 2\text{CO}_2 \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$	Produces acetate and can alter pH/alkalinity, affecting long-term biogeochemistry.
	Sulfate reduction (<i>sulfate reducing bacteria</i>)	$\text{SO}_4^{2-} + 4\text{H}_2 + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$	Generates H_2S (toxic/corrosive), potential for sulfide mineral precipitation or souring.
	Dissimilatory Fe(III) reduction (<i>dissimilatory iron-reducing bacteria, e.g., Geobacter and Shewanella spp.</i>)	$2\text{FeOOH} + \text{H}_2 + 4\text{H}^+ \rightarrow 2\text{Fe}^{2+} + 4\text{H}_2\text{O}$	Couples H_2 oxidation to ferric-iron reduction in anoxic deep-subsurface settings, consuming H_2 and generating aqueous Fe^{2+} that can drive secondary mineral precipitation (siderite, magnetite, or mackinawite where sulfide is co-present) and modify pH and Eh.
Geochemical	Fe(III) reduction (<i>abiotic, redox-sensitive minerals</i>)	$\text{Fe}_2\text{O}_3 + 3\text{H}_2 \rightarrow 2\text{Fe} + 3\text{H}_2\text{O}$	Consumes H_2 locally, can modify mineralogy, porosity/permeability, and interfacial properties.

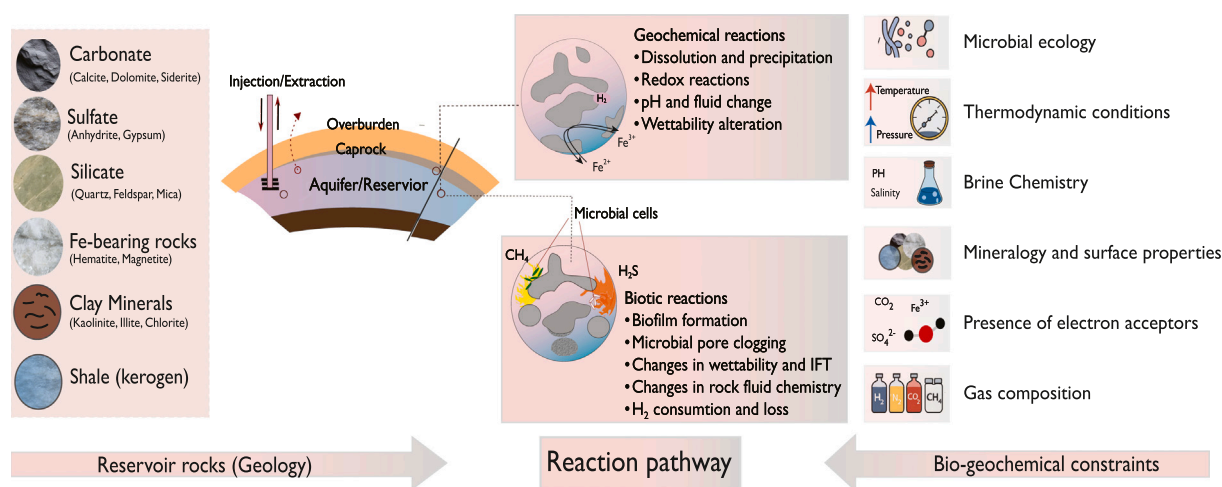


Fig. 11. (Left) Representative mineral groups within seal and reservoir systems, including carbonates (calcite, dolomite, siderite), sulfates (anhydrite, gypsum), silicates (quartz, feldspar, mica), Fe-bearing oxides (hematite, magnetite), clay minerals (kaolinite, illite, chlorite), and organic-rich shale (kerogen), interacting with the hydrogen-brine interface. (Centre) Associated reaction pathways encompassing geochemical reactions and microbial interactions. (Right) Key variables and constraints influencing reaction pathways. The figure is intended as a process map in which mineralogy defines possible reaction pathways, while constraints (such as temperature, redox state, microbial communities, etc.) regulate whether those pathways meaningfully affect gas quality, permeability, and storage integrity.

Injecting hydrogen into subsurface formations can trigger a spectrum of biotic and abiotic pathways involving redox transformations, microbial hydrogenotrophy, mineral dissolution and precipitation, and surface conditioning. Current understanding indicates that the impacts on UHS performance cluster into three recurring mechanisms, summarized in Table 8 and conceptually illustrated in Fig. 11, which together highlight how mineralogy, microbial activity, brine chemistry, and reservoir conditions collectively shape these interactions and their outcomes. First, hydrogen can be consumed while secondary gases such as CH_4 and H_2S are generated, reducing recoverable hydrogen and degrading purity [17,42,128]. Second, interfacial properties can shift through biofilm growth, accumulation of extracellular polymeric substances (EPS), adsorption of reaction products, and secondary mineral coatings, which can alter wettability and capillary thresholds and thus reshape trapping and remobilization [62,88,188]. Third, pore structure can evolve through mineral dissolution or precipitation, modifying pore throat distributions and connectivity, with implications for permeability, flow redistribution, and long-term storage integrity [16,128,199]. Building on this framework, the following sections first examine microbial interactions capable of producing rapid changes in gas composition and interfacial behaviour, and then consider abiotic reactions that become relevant under specific lithological and geochemical conditions.

3.1. Microbial interactions

Microbial activity is frequently cited as a major uncertainty in UHS because hydrogen serves as an energetically favourable electron donor under anaerobic conditions. In UHS systems, microbes can metabolize hydrogen through methanogenesis, acetogenesis, sulfate reduction, and dissimilatory Fe(III) reduction, consuming electron acceptors such as CO_2 , SO_4^{2-} , and ferric-iron-bearing minerals and producing secondary species including CH_4 , CH_3COOH , H_2S , and aqueous Fe^{2+} (Table 8, [159,180]). Experimental observations that document these pathways and their operational implications for UHS, including hydrogen loss, secondary gas generation, and impacts on produced-gas purity, are synthesized in Table 9. These studies span a wide range of methodologies, from controlled batch reactors used to quantify hydrogen consumption through the aforementioned pathways, to more advanced systems such as microfluidic devices, micromodels, and high-pressure core-flood experiments. These approaches enable not only the assessment of microbial activity under controlled temperature, pressure, and salinity conditions, but also direct visualization of biofilm growth, multiphase displacement, and measurements of changes in wettability and interfacial tension.

As microbial activity can directly alter gas composition while modifying hydrogen transport and storage dynamics, resolving the occurrence

Table 9
Synthesis of key studies examining hydrogen-microbe interactions relevant to UHS.

Study Objective	Rock formation	Gas composition	Microbiome	Key findings	Refs
Impact of microbial activity on wettability under UHS conditions	Bentheimer sandstone and quartz	hydrogen	Living brine (<i>Oleidesulfovibrio alaskensis</i>)	Contact-angle measurements using the captive-bubble method at 3 bar and 37 °C, biofilm formation altered wettability depending on surface roughness. Contact angles remained unchanged on rough Bentheimer sandstone but decreased significantly on smooth quartz, indicating increased water-wetness and highlighting the role of surface texture and biofilm morphology.	[40]
Gas-brine and microbial interactions	Deep aquifers / core samples / formation water	1% CO ₂ + CH ₄ , 10% hydrogen + CH ₄	Autochthonous microbiome	High-pressure batch experiments (85.8 bar to 95 bar, 47 °C), Microbial hydrogen consumption caused substantial gas losses in calcite-rich, sulfate-bearing aquifers and was accompanied by dissolution of calcite (CaCO ₃) and barite (BaSO ₄), indicating biogenic alteration of reservoir mineralogy.	[84]
Wettability changes under geostorage conditions	Sandstone reservoirs / quartz substrates / nutrient medium and brine	hydrogen	Sulfate-reducing bacteria (21-day ageing)	Contact-angle measurements up to 270 bar and 50 °C, SRB biofilms shifted wettability toward less water-wetness, with no observable alteration of quartz surface morphology.	[3]
Microbial biofilm effects on wettability	Sandstone reservoirs (pristine and aged quartz) / synthetic brine	hydrogen (3–130 bar, 25–50 °C)	Cyanobacteria (<i>Geitlerinema</i> sp.)	Microorganisms modified sandstone wettability and interfacial properties, with the magnitude and direction of change dependent on initial surface condition and rock history.	[17]
Methanogenic conversion of hydrogen and CO ₂	Depleted gas reservoirs / drill cores / reservoir water	10% hydrogen, 2.5% CO ₂ + CH ₄	Autochthonous methanogens	Bioreactor experiments (39–45 bar, 40 °C), microbial community analysis showed hydrogen conversion linked to indigenous microbes under in situ-like geochemical conditions.	[92]
In situ hydrogen consumption	Natural gas field / formation fluid	0.4–10% hydrogen + N ₂ , 1–2% CO ₂	Autochthonous sulfate-reducing microbes	Batch and high-pressure reactors (ambient–100 bar, 30–60 °C), hydrogen depletion rates correlated with microbial activity and sulfate availability as a terminal electron acceptor.	[58]
Extent and rates of hydrogen consumption under hypersaline conditions	Hypersaline reservoirs / nutrient medium / cavern brine	10–100% hydrogen + 5–20% CO ₂ + N ₂	Halophilic sulfate-reducing microbes	Batch experiments at 30–37 °C, hydrogen consumption (up to 12%) and sulfide formation observed under hypersaline conditions. The resulting pH increase progressively suppressed microbial activity, favouring hydrogen preservation in salt caverns.	[62]
Hydrogen consumption and wettability alteration	Sandstone reservoirs / silicon micromodel / growth medium	hydrogen	Halophilic sulfate-reducing bacteria	Microfluidic experiments (35 bar, 37 °C), biofilm growth altered pore-scale wettability, reducing water-wetness from 41° to 94°, compared with a nearly constant contact angle of 45° in sterilized controls.	[128]
Biogeochemical alteration of wellbore cement and shale under hydrogen storage conditions	Class H wellbore cement cores with Marcellus and Woodford shale	H ₂ (95%) ± CO ₂ (5%), 100 bar, 60 °C, 16 weeks	Indigenous microbial consortia introduced via shale and synthetic formation brine	Hydrogenotrophic microbial activity consumed H ₂ and generated CH ₄ and H ₂ S. CO ₂ buffered pH, promoted cement carbonation, and enabled retention of reduced S and Fe as carbonate-associated phases, while shale acted primarily as an inoculum and nutrient source without undergoing detectable mineral alteration.	[161]
Microbial growth in two-phase media and validation of a modified Monod model	Glass-silicon micromodel representing Bentheimer sandstone pore geometry	80% hydrogen + 20% CO ₂	Methanogenic archaea (<i>Methanolacinia petrolearia</i> , <i>Methanothermococcus thermolithotrophicus</i>)	Micromodel experiments (1.1–1.75 bar, 37–63 °C) showing microbial growth occurred predominantly at the gas-liquid interface.	[175]
Field-scale demonstration of biomethanation in depleted underground gas storage	Depleted reservoir	Hydrogen + CO ₂ (4 to 1) injected into formation fluid	Autochthonous microbial community dominated by hydrogenotrophic methanogens	Hydrogen injection rapidly shifted the microbial community toward methanogens (from 1% to 43% of total abundance within days), demonstrating in-situ methane production without external inoculation.	[189]
Microbial influence on wettability and interfacial properties	Basalt formations	hydrogen	Sulfate-reducing bacteria	Experiments conducted at room temperature and 25–50 °C up to 4000 psi, microbial inoculation reduced interfacial tension by ~ 19% and capillary pressure by ~ 65%, with an upward shift in contact angle indicating reduced water-wetness and potentially enhanced hydrogen mobility.	[4]
Impact of microbial activity and biofilm formation on multiphase flow during UHS	Bentheimer sandstone cores / multiphase core-flood experiments	hydrogen	Biofilm-producing microbial culture	Microbial colonization reduced water-wetness toward neutral conditions, improved pore accessibility, increased gas saturation, and enhanced displacement efficiency, with implications for trapping and hydrogen loss.	[166]
Microbial hydrogen consumption in salt cavern brines	High-salinity brine	Hydrogen-amended incubations with and without nutrient addition	Halophilic microbial community	At 30 °C, sulfate-reducing activity occurred even without nutrient enrichment, producing H ₂ S and elevating pH. Microbes persisted under extreme salinity, but hydrogen loss was minimal in the absence of nutrient input.	[64]

and intensity of these pathways is essential for predicting hydrogen losses and gas-quality evolution in porous media. Reported optimal temperature ranges for acetogenesis, methanogenesis, and sulfate reduction are typically 20 °C to 30 °C, 30 °C to 40 °C, and 20 °C to 30 °C, respectively, although many microbial communities operate across broader thermal envelopes. These processes generally proceed most efficiently near neutral pH (~ 6.0–7.5), with tolerance extending beyond this range depending on community composition and brine chemistry. Salinity constraints are similarly pathway-specific, with acetogens often reported below 40 g L⁻¹, methanogens below 60 g L⁻¹, and sulfate reducers below 100 g L⁻¹, while documented exceptions occur in hypersaline environments. For example, Dopffel et al. [64] demonstrated that sulfate-reducing communities can persist under extreme salinity, although with gradual hydrogen consumption ultimately constrained by pH feedback. Microfluidic and batch experiments by Liu et al. [128] and Boon et al. [42] further show that microbial activity is highly sensitive to brine salinity, temperature, and electron acceptor availability.

As a result of these sensitivities, hydrogen consumption by native microbial communities in formation water collected on-site can vary markedly during laboratory experiments. Reported observations range from negligible hydrogen consumption [187], to immediate hydrogen uptake without nutrient addition, to sustained multi-cycle biomethanation under favourable conditions [58]. Across these studies, hydrogen consistently emerges as a major energy source for subsurface microbial communities, particularly under anaerobic conditions where hydrogenotrophic pathways dominate. To connect microbial pathways to multiphase flow outcomes, we group the reported impacts into wettability alteration, hydrogen consumption and saturation dynamics, and mineral and pH feedbacks.

3.1.1. Wettability alteration

Microbial utilization of hydrogen can promote biofilm formation on mineral surfaces, leading to the production of EPS and the release of organic metabolic by-products. These processes can modify surface chemistry and, in some cases, locally reduce pH, thereby altering mineral-fluid interactions [40]. Depending on biofilm composition, surface roughness, and environmental conditions, such alterations may either enhance hydrophilicity or promote more hydrophobic surface behaviour, with direct consequences for fluid distribution, mobility, and capillary trapping in porous media [128].

Wettability changes driven by hydrogen-rock-microbe interactions are typically evaluated through contact angle measurements before and after microbial activity. Liu et al. [128] used a microfluidic silicon micromodel replicating sandstone pore geometry inoculated with halophilic sulfate-reducing bacteria and observed a marked reduction in water-wetness, with average contact angles increasing from 41° to 94°. In contrast, sterilized control experiments exhibited minimal change, with contact angles remaining near 45°. These results demonstrate that biofilm growth can substantially modify interfacial conditions, sufficient to shift capillary entry pressure and trapping behaviour, which are central to the hysteresis and cyclic efficiency discussed earlier.

The magnitude and direction of wettability alteration are further modulated by biofilm morphology and substrate texture. Using a captive-bubble method at 3 bar and 37 °C, Boon et al. [40] measured contact angles on Bentheimer sandstone and quartz surfaces in brine inoculated with *Oleidesulfovibrio alaskensis*. While wettability remained largely unchanged on rough Bentheimer sandstone, contact angles on smooth quartz decreased significantly, indicating increased water-wetness. Similarly, Ali et al. [17] showed that microbial alteration of wettability and interfacial properties correlates with the initial surface state, indicating that rock history and prior conditioning can control the extent of wettability alteration. Reported trends across studies remain mixed. Aftab et al. [4] reported reductions in interfacial tension by 19% and capillary pressure by 65%, accompanied by a shift toward less water-wetness, consistent with Ali et al. [18] and Aftab et al. [3]. In contrast, Al-Yaseri et al. [14] observed increased hydrophilicity in

Berea sandstone attributed to the consumption of carboxylic acid groups, which increased capillary pressures and residual water saturations while leaving interfacial tension largely unchanged.

3.1.2. Hydrogen consumption, saturation dynamics, and fluid mobility

Hydrogen consumption is one of the most consequential outcomes of biogeochemical interactions during subsurface storage and can occur spontaneously [80,186]. Dopffel et al. [64] documented hydrogen uptake by halophilic microbial communities under high salinity, nutrient limited conditions. Core-scale experiments by Shiran et al. [166] similarly confirmed microbial activity as a driver of gas consumption. At larger scales, Vítězová et al. [189] showed that co-injection of hydrogen and CO₂ into depleted reservoirs can stimulate indigenous methanogens and produce substantial biomethanation.

Microbes can also influence saturation distributions and displacement efficiency by reshaping interfacial conditions and pore accessibility. Shiran et al. [166] found that microbial colonization reduced water-wetness toward near-neutral conditions, improved pore accessibility, increased hydrogen gas saturation, and enhanced displacement efficiency. Similarly, micromodel experiments by Strobel et al. [175] demonstrated preferential colonization at the gas-liquid interface by *methanogenic archaea*, indicating that interfacial regions act as microbial hotspots. This localized biofilm growth can redistribute fluid pathways and modify multiphase flow dynamics. Complementary pore-scale experiments by Liu et al. [128] showed that microbial activity accelerated gas disconnection into isolated bubbles. Under microbial activity, disconnected gas saturation reached 72.8% within 5 hours, compared with 22.6% in sterilized controls. This behaviour was coupled to biofilm-driven wettability changes that reduced capillary entry pressure and enabled hydrogen migration into smaller pores. While such redistribution can increase apparent invaded volume, it can also increase the fraction of immobile disconnected gas and enhance microbial consumption of isolated clusters, thereby lowering hydrogen recovery.

3.1.3. Mineral dissolution and pH changes

Microbial metabolism and its associated by-products can induce substantial mineralogical and geochemical changes that feed back into pore structure and permeability evolution. Using high-pressure batch experiments (85–95 bar, 47 °C) on deep aquifer samples containing indigenous microbial communities, Haddad et al. [84] showed that microbial hydrogen consumption was coupled to the dissolution of calcite (CaCO₃) and barite (BaSO₄), consistent with biogenic acidification altering reservoir mineralogy. Similarly, Rooney et al. [161] demonstrated that microbially mediated sulfate and iron reduction in wellbore cement led to the generation of CH₄ and H₂S, degrading cement mineral phases, particularly within diffusion-limited zones, and directly compromising well integrity and produced-gas purity. In hypersaline systems, Dopffel et al. [62] observed that halophilic sulfate reducers consumed up to 12% of injected hydrogen, producing sulfide and increasing pH to levels that eventually suppressed microbial activity.

Beyond direct hydrogen loss, sulfate-reducing bacteria can substantially modify brine chemistry and promote secondary mineral formation. Experimental investigations document pronounced pH shifts and sulfate depletion associated with microbial metabolism, conditions that are conducive to mineral precipitation in natural reservoir systems [63,166]. Direct evidence for such processes under UHS-relevant conditions was provided by Aftab et al. [3], who observed extensive mineral precipitation during hydrogen-brine-rock interaction experiments. In these systems, microbial sulfate reduction resulted in nearly 80% removal of dissolved Fe and 40–50% reductions in Ca and Mg concentrations due to the precipitation of insoluble sulfide phases (FeS, CaS, MgS).

Microbially catalyzed redox reactions can further enhance mineral precipitation, and under conditions where dissolved iron coexists with nitrate or low oxygen availability, iron-oxidizing microorganisms may precipitate ferric phases such as goethite or magnetite [62]. These geochemical transformations can also modify pore structure and flow

behaviour. A major physical consequence is bioclogging, whereby the accumulation of microbial cells, biofilm, and extracellular polymeric substances (EPS) progressively occupies pore bodies and constricts pore throats, reducing effective porosity, permeability, and injectivity [62, 188]. This permeability reduction is typically spatially heterogeneous rather than uniform and is most pronounced where electron donors, electron acceptors, and nutrients coexist, particularly near the injection well and along the gas-water interface, where micromodel experiments have documented preferential biomass colonization [128,175]. Its magnitude depends on nutrient and electron-acceptor availability, salinity, temperature, shear rate, and pore structure, and may become self-limiting where nutrients are depleted or where metabolic by-products such as elevated pH or H₂S suppress further microbial activity [62].

Bioclogging is also expected to evolve dynamically during cyclic operation, as shear during injection and withdrawal, pressure and saturation fluctuations, and near-wellbore desiccation may detach biofilm and permit partial permeability recovery, whereas repeated nutrient supply may sustain renewed growth. The magnitude, spatial extent, and reversibility of these effects under realistic cyclic UHS conditions remain poorly constrained and require dedicated long-term flow-through experiments [88,166]. These studies indicate that microbially mediated mineral dissolution, precipitation, and pH-driven geochemical alteration represent important controls on porosity evolution, reservoir integrity, and long-term storage security in UHS.

3.2. Abiotic geochemical reactions

In addition to microbial metabolism, hydrogen can participate in abiotic reactions that alter reservoir geochemistry and mineralogy. These reactions are governed by hydrogen's strong reducing potential, the availability of electron acceptors, reservoir temperature and pressure, and formation fluid composition [188]. Because hydrogen is buoyant, it often accumulates beneath the caprock, and persistent hydrogen-brine contact can occur near gas-water transition zones. Similarly, due to its wetting behaviour, hydrogen preferentially occupies the larger pore spaces of the host rock, where it comes into contact with both formation fluids and the mineral matrix [98,106,112]. Within this coupled rock-fluid-gas system, abiotic reactions may drive dissolution and precipitation, modify reactive surface area, and in some cases consume hydrogen locally, with implications for porosity, permeability, and long-term integrity [88]. Only a limited number of experiments have quantified hydrogen-fluid-rock interactions and their associated geochemical effects, as summarized in Table 10.

Generally, hydrogen-driven abiotic alteration depends strongly on the mineral phases it interacts with. In sandstone reservoirs, reactivity is low due to the thermodynamic stability of silicate-rich rocks [73,89]. Batch and core exposure tests commonly report negligible mineral alteration and no measurable hydrogen loss over weeks to months under elevated pressure and temperature conditions [73]. Hassanpouryouzband et al. [89] reported results from 250 batch experiments across multiple sandstone lithologies and found negligible differences in fluid chemistry between H₂-rich and N₂-rich controls over two months, supporting the conclusion that abiotic reactions exert only a minor influence in many sandstone settings. These experimental findings are further supported by reactive transport models, which predict negligible hydrogen losses in quartz-rich formations [39,199]. Meanwhile, carbonate minerals (e.g., dawsonite, calcite, dolomite, siderite) can be more sensitive because carbonates respond readily to aqueous chemistry changes triggered by hydrogen-rock-water interactions. Many short-term studies still report limited or balanced dissolution-precipitation effects. Bensing et al. [34] documented dissolution of calcite fossil fragments in claystone shale exposed to hydrogen-saturated brine (10 wt% NaCl), highlighting the potential for caprock alteration.

In addition, Zeng et al. [200] showed that carbonate minerals undergo redox-driven transformations to CH₄, which pose a potential risk, particularly in depleted hydrocarbon-bearing carbonate reservoirs.

Dodangoda et al. [57] reported minor calcite dissolution, but observed that at high water-to-rock ratios (W/R) hydrogen loss could reach 25% within 10 days, accompanied by substantial porosity increases (up to 63%). In contrast, other studies report negligible reactivity under similar conditions. For example, Al-Yaseri et al. [11] exposed pure calcite limestone samples to hydrogen at 1500 psi and 75 °C for 6–13 months and detected no secondary gases (such as CH₄) and no clear evidence of hydrogen-calcite reaction. Al-Yaseri et al. [13] reported near-balanced dissolution and precipitation of calcite and dolomite over 150 days at 9.7 MPa and 75 °C, with porosity changes ≤2%, suggesting limited early-cycle impact in some carbonates.

Redox-sensitive minerals, particularly Fe-bearing oxides such as hematite, may undergo reduction under hydrogen exposure, with ferric iron (Fe³⁺) converted to ferrous iron (Fe²⁺). In addition, several studies suggest that pyrite reduction can occur under hydrogen-rich conditions, highlighting the potential for hydrogen-driven redox transformations in subsurface environments [171,183]. Consistent with this, Yekta et al. [199] demonstrated hydrogen-driven redox reactions involving Fe-bearing phases, including hematite, Fe-rich micas, and clays. The dissolution of redox-sensitive phases can liberate electron acceptors (e.g., Fe³⁺), which may subsequently couple with microbial pathways, potentially influencing hydrogen availability and promoting secondary mineral precipitation [56]. Sulfate-bearing minerals can be reactive under specific temperature, pressure, and water saturation conditions. Anhydrite is generally stable under ambient conditions but may dissolve or re-equilibrate at elevated temperatures and pressures, particularly in the presence of high water saturation and specific ionic environments, potentially producing H₂S. Fleisch et al. [73] observed that the dissolution of pore-filling anhydrite minerals can increase porosity and permeability by enlarging existing pore networks.

Clay minerals, particularly illite and kaolinite, are also common in both reservoir rocks and caprocks and contribute significantly to rock surface area. Aldhuhoori et al. [16] observed low but measurable dissolution of illite and kaolinite (2.17% and 3.01%, respectively) under hydrogen exposure, suggesting that while some degree of mineral dissolution may occur, it is unlikely to be geochemically significant compared with the influences of water chemistry, temperature, and the presence of other reactive species. Even so, hydrogen can be weakly physisorbed onto clay surfaces or accommodated within micropores. In expandable clays, water uptake can induce swelling-related stress changes that influence permeability and seal integrity [91].

Beyond single-gas systems, cushion gases can shift aqueous chemistry and reaction rates. Exposure to hydrogen with CO₂ can enhance carbonate reactivity and influence injectivity or sealing capacity [10,68,70]. However, many of these reactions require extreme conditions (high pressure, temperature, and salinity) and long timescales that are not typical of most UHS reservoirs [70,156]. Overall, current evidence indicates that abiotic effects are generally minor in the absence of microbial activity [16,43,80]. Although many abiotic pathways are thermodynamically favourable, they often proceed slowly under typical reservoir conditions. The predicted dissolution of shale minerals can remain below 1% over 30-year timescales [201]. By contrast, microbial processes can catalyze and accelerate transformations, amplifying both geochemical significance and operational impact, consistent with the discussion in Section 3.1. This coupling underscores the need for site-specific characterization of mineralogy, fluid composition, electron acceptor availability, and microbial ecology, alongside monitoring strategies that can detect evolving gas composition and changes in injectivity and deliverability.

Most experimental findings on pristine target formations indicate that hydrogen alone does not strongly alter mineralogy or wettability. Where significant changes are observed, they are commonly associated with external controls such as temperature, pressure, salinity, organic matter content, and microbial activity [107]. In many settings, the dominant uncertainty is not hydrogen in isolation, but the extent to which biogeochemical feedback drives the time-dependent evolution of

Table 10
Summary of hydrogen-rock-brine abiotic interaction studies.

Study Objective	Rock Type	Fluids studied	Conditions and Methods	Key findings	Refs
Caprock alteration under hydrogen exposure	Claystone caprock proxies	hydrogen/brine	10 wt% NaCl, ~30 days, static tests, SEM imaging	Calcite fossils dissolved only under combined hydrogen-brine conditions, suggesting that carbonate-rich caprocks containing fossil textures may undergo localized dissolution during hydrogen-brine contact.	[34]
Effect of hydrogen on calcite reactivity in sandstone	Calcite-bearing sandstone	hydrogen, N ₂ , distilled water	100 bar, 105 °C, 78 h, experimental study & modelling	Calcite remained largely unreactive under exposure to hydrogen, while thermodynamic calculations tended to overpredict both dissolution and hydrogen loss.	[78]
Petrophysical change during hydrogen exposure	Reservoir sandstones (21 cores)	100% hydrogen	Up to 6 weeks, reservoir conditions, batch tests & micro-CT	Overall negligible alterations, quartz/silica-cemented sandstones are geochemically robust for early UHS cycles.	[73]
Large campaign on abiotic reactivity in sandstones	Various reservoir sandstones (~250 batch tests)	hydrogen vs. controls	batch experiments with controls	No evidence of abiotic hydrogen loss or integrity degradation was found in sandstones.	[89]
Hydrogen reactivity and petrophysical impacts	Buntsandstein sandstones (pyrite-free)	Hydrogen/synthetic brine, air	150 bar, 100 °C, 4 weeks, batch tests, fluid chemistry	No significant hydrogen-driven mineralogical changes, minor ϕ/k shifts from anhydrite disequilibrium.	[49]
Hydrogen-clay interactions with micro-CT verification	Bandera and Berea sandstones	Hydrogen + 30% brine	9.7 MPa, 75 °C, 75 days, core tests & micro-CT porosity	Negligible geochemical alteration with stable porosity/clay content ($\Delta\phi \leq 0.1\%$). No quartz/clay dissolution.	[15]
Basalt-hydrogen-water interactions & property impacts	Basalt (CarbFix, Iceland)	hydrogen + DI water	9.65 MPa, 75 °C, 108 days, SEM & petrophysics	Basalt showed low reactivity with minor plagioclase dissolution. Surfaces remained water-wet, supporting containment and predictable relative permeability.	[12]
Effect of CO ₂ cushion gas on pore properties	Indiana Limestone and Bandera Grey Sandstone	Hydrogen-CO ₂ mixture	9.7 MPa, 75 °C, 90 days, petrophysical analysis	Porosity increased 6–10% and permeability 10–14%. CO ₂ cushion gas may enhance injectivity, but long-term reactivity and seal performance need monitoring.	[70]
Long-term carbonate/hydrogen behaviour and hydrogen loss	Carbonate-rich rocks	hydrogen (N ₂ controls), variable W/R	2.8–12 MPa, 28–70 °C, up to 180 days, XRD, SEM, CT, fluid chemistry	Average reactivity limited (~1% calcite dissolution, ~1% mineral precipitation), but hydrogen loss reached 25% in 10 days at high W/R. CT showed porosity increase up to 63%.	[57]
Hydrogen ageing in dolomite reservoirs	Dolomite (Blina Field, Australia)	hydrogen + synthetic brine	4.14 MPa, 50 °C, 120 days, SEM & XRD	Dolomite dissolution and ankerite precipitation with strong TOC loss (~56%). Permeability rose 20% in porous samples. Delayed CH ₄ release indicated elevated hydrogen loss risk in organic-rich carbonates.	[53]
Hydrogen effects on shale	Eagle Ford (medium TOC) and Wolfcamp (low TOC) shales	hydrogen + 3 wt% NaCl brine	9.65 MPa, 75 °C, 108 days, SEM, porosity, permeability tests	Calcite precipitation (likely from organic-derived CO ₂) occurred post-hydrogen exposure. No sulfate or pyrite reduction. Seal integrity intact, minor pore changes.	[6]

the interfacial and petrophysical parameters that control trapping and cyclic recovery. Unlike hydrogen, CO₂ has higher solubility in brine and stronger geochemical reactivity, so mixed-gas operation and cushion gas selection can play a major role in long-term interfacial evolution and rock-fluid interactions.

4. Cross-scale synthesis and limitations in the current understanding of UHS

Despite substantial advances in multiphase flow-dominated and biogeochemical studies, understanding and prediction of UHS remain fragmented. When viewed collectively, unresolved challenges arise not from isolated uncertainties but from a structural mismatch between pore-scale physics, evolving interfacial chemistry, biogeochemical feedback, and reservoir-scale operational dynamics. Most studies implicitly assume static wettability, rate-invariant displacement, homogeneous pore structure, and weakly coupled reactions. However, hydrogen storage is inherently a non-stationary, cyclic, multicomponent, and reactive multiphase process. This disconnect between simplifying assumptions and physical reality is a primary reason why laboratory findings remain difficult to upscale reliably to field-scale design.

4.1. Dynamic wettability and interfacial energies

While hydrogen-brine interfacial tension (γ) is relatively well constrained, the solid-fluid interfacial energies that ultimately govern wettability are rarely measured directly and are instead inferred from thermodynamic models. This reliance on indirect estimates limits

mechanistic insight into how hydrogen interacts with heterogeneous, mineralogically complex reservoir surfaces. Most experiments rely on idealized mineral substrates such as quartz or mica, whereas candidate storage formations are commonly heterogeneous, clay-rich, or chemically altered [6,9]. The influence of clay mineral variability on wettability evolution and trapping efficiency therefore remains poorly constrained, particularly where long-term mineral transformation or secondary phase formation may occur, and where impurities such as CO₂, CH₄, and H₂S modify surface chemistry and brine composition [72]. These effects have direct implications for permeability evolution, sealing integrity, and capillary trapping.

Crucially, wettability in UHS reservoirs should be treated as a dynamic, history-dependent state variable controlled by mineralogy, impurities, microbial activity, and cyclic pressure-temperature-composition trajectories. Yet, many studies continue to assume fixed contact angles and interfacial tensions, despite growing evidence that these parameters evolve with salinity, pressure, temperature, and bio-geological activity. This simplification limits predictive capability, particularly under cyclic injection-withdrawal conditions where transient wettability shifts may progressively alter trapping behaviour and hydrogen mobility.

4.2. Rate-dependent displacement, heterogeneity, and representativeness of laboratory systems

Another central unresolved issue relates to the assumption of rate-invariant hydrogen displacement. Most studies examine drainage or imbibition in isolation, despite strong rate dependence in both processes,

influencing both sweep efficiency and residual trapping. Experimental studies have shown that injection and withdrawal rates exert first-order control on displacement efficiency, with low injection combined with high withdrawal enhancing pore-space utilization, whereas high injection rates promote preferential flow and reduce residual trapping [193]. However, these findings are derived from homogeneous, centimeter-scale samples under laboratory conditions, leaving their applicability to heterogeneous reservoirs under field-relevant stress, temperature, and pressure unresolved. Quantitatively, a complete description of cyclic UHS requires placing the cycle period against the relaxation times of pore-pressure equilibration, OR-driven redistribution, and microbial activity, and complementing the static Ca , M , and N_g introduced in Section 2 with a Damköhler-like ratio of cycle period to reaction time and a Strouhal-like ratio of cycle frequency to advection time. Such time-domain framings remain largely absent from the literature and represent an important target for future experimental, modelling and scaling studies.

Hydrogen displacement is often described as capillary dominated, yet this assumption fails to capture rate-sensitive pore-scale instabilities. Time-resolved imaging in Clashach sandstone shows that even at low Ca , hydrogen advances through intermittent bursts and sudden pore-filling events (Haines jumps) accompanied by pressure oscillations [178]. Synchrotron tomography further reveals that non-wetting phase mobility is elevated during transient flow relative to steady state, with intermittency closely linked to this behaviour [172]. These dynamics demonstrate that displacement cannot be described solely by stable capillary invasion, as local viscous effects and pore-scale instabilities strongly influence saturation and trapping. Yet, most reservoir-scale models neglect such rate-sensitive, energy-dissipating processes, limiting predictive accuracy for injectivity and recovery. Compounding this issue is the wide scatter in reported initial and residual gas saturation across experimental studies. Outcomes depend strongly on boundary conditions, sample preparation methods, pore structure representation, and the measurement stage (breakthrough versus steady state). This variability complicates inter-study comparisons and undermines generalization of trapping efficiency from saturation data alone.

A further limitation of the UHS evidence base is the dominance of homogeneous sandstone cores and simplified pore networks. The influence of dual-porosity systems, stratification, and natural fractures remains poorly constrained, despite their strong control on gas connectivity, residual trapping, and cyclic recovery. Chemically reactive lithologies, such as clay-rich formations and basaltic reservoirs, despite their abundance and favourable permeability, have received limited systematic attention. Their complex mineralogy, bimodal pore structures, and reactive surfaces introduce uncertainties in wettability evolution and trapping behaviour that differ fundamentally from conventional sedimentary rocks [106]. The large scatter in saturation data further highlights the limitations of relying on porosity and permeability alone to predict trapping efficiency. While traditional petrophysical parameters capture part of the variability, they cannot fully explain observed discrepancies across different rock types and experimental conditions. Integrative descriptors such as the Reservoir Quality Index (RQI) and Flow Zone Indicator (FZI) have successfully linked pore structure to flow behaviour in hydrocarbon systems, yet remain largely unexplored for hydrogen-brine systems. Incorporating such metrics into UHS workflows could improve cross-scale comparability and reduce inconsistencies across studies.

A further limitation of laboratory representativeness is the treatment of geomechanical conditions. Most hydrogen core-flood experiments are conducted under static confining pressure, whereas field-scale UHS operations involve repeated injection and withdrawal cycles that generate fluctuating pore pressures and cyclic effective stresses. These stress variations can alter pore structure, induce cumulative grain-scale damage, reactivate pre-existing faults, and increase the potential for hydrogen leakage and induced seismicity [167,184]. Similar effects have been observed in salt caverns, where cyclic loading influences

elastic properties, short-term strength, and viscoplastic creep behaviour [121]. Geomechanical responses may be further amplified by hydrogen-induced geochemical alteration. For example, Dabbaghi et al. [51] reported reductions of up to 41% in peak strength, 43% in elastic modulus, and 23–63% in internal friction angle for hydrogen-exposed Hulett sandstone, accompanied by dolomite and clay dissolution. However, reported responses remain highly lithology dependent. Quartz-rich sandstones generally retain greater stiffness than clay- and carbonate-rich formations [105], whereas some limestones have exhibited increases in Young's modulus following short-term hydrogen exposure [75]. In contrast, longer-term sandstone-brine experiments have shown only minor geochemical alteration and negligible changes in elastic properties [181]. These contrasting observations indicate that hydrogen-induced chemo-mechanical effects depend strongly on mineralogy, brine composition, and stress history. Consequently, conventional static-pressure core-flood experiments cannot adequately capture the coupled cyclic-stress and geochemical processes governing long-term reservoir integrity, highlighting the need for dedicated cyclic-loading experiments.

4.3. Cyclic hysteresis, Ostwald ripening and time-dependent redistribution

Cyclic injection and withdrawal are intrinsic to UHS operations, yet hysteresis behaviour remains poorly resolved. Some studies report stabilization of residual saturation after only a few cycles, suggesting convergence toward a hysteretic equilibrium [197], whereas others document a progressive accumulation of residual hydrogen with no clear stabilization. These divergent outcomes raise fundamental questions regarding whether cyclic hysteresis tends toward equilibrium or accumulates irreversibly over storage time. This lack of consensus is exacerbated by the limited number of cycles explored experimentally, usually fewer than five, and by the strong sensitivity of hysteresis behaviour to boundary conditions.

Dynamic wettability during cyclic flow represents an additional source of uncertainty. Although contact-angle hysteresis has been observed, the controlling mechanisms, including film swelling, surface roughness, mineral alteration, and biofilm development, remain unresolved. The role of hydrogen dissolution is also rarely isolated, complicating the distinction between physical hysteresis and chemically driven effects. Most experiments rely on pristine mineral surfaces, whereas long-term storage conditions involve impurities, microbial activity, and evolving brine chemistry that may progressively modify hysteresis behaviour [106]. Under these conditions, cyclic UHS behaviour should be regarded as non-stationary and history dependent, rather than converging toward a unique steady state.

Ostwald ripening has been increasingly recognized as relevant to UHS, yet key uncertainties persist. Most studies focus on pure gas systems, whereas practical UHS operations often involve gas mixtures, either by design, such as cushion gases (N_2 , CH_4), or as residual formation gases in depleted hydrocarbon fields. Multicomponent systems introduce additional complexity because each gas exhibits distinct solubility, diffusivity, and interfacial properties, potentially driving preferential mass transfer and time-dependent redistribution of hydrogen. The relative contribution of each gas to coarsening kinetics also remains poorly constrained, and experimental evidence for the evolution of compositional heterogeneity during cyclic injection-withdrawal is still lacking.

Scaling Ostwald ripening from the pore to the reservoir scale represents another major uncertainty. While laboratory and imaging studies consistently demonstrate short-term remobilization, it remains unclear whether these transient pore-scale behaviours persist, average out at macroscopic flow scales, or meaningfully influence residual saturation, hysteresis, and relative permeability. This question has been explored in only a few studies [82,170]. Whether such remobilization enhances recovery or undermines containment by destabilizing residual trapping therefore remains an open question. Ostwald ripening should thus not be treated as an isolated pore-scale curiosity, but as a time-dependent

redistribution mechanism that interacts with hysteresis, multicomponent dissolution-exsolution, and cyclic displacement.

4.4. Biogeochemical coupling and long-term storage integrity

Although abiotic reactions between hydrogen and reservoir minerals are generally limited under typical subsurface conditions, mineral-specific reactivity, brine composition, and cyclic operation introduce significant variability that is not yet well constrained. Quartz-rich sandstones appear largely inert [73,89], whereas carbonate and redox-sensitive minerals show more variable responses, including dissolution, secondary mineral precipitation, and measurable hydrogen loss [57]. These results remain highly inconsistent, with some studies reporting no detectable reactions even after long exposure [15], while others report up to 25% hydrogen loss within days under high water-to-rock ratios. This disparity reflects a lack of standardized experimental protocols and the need for more representative long-term datasets under reservoir-relevant conditions.

In contrast, laboratory studies consistently demonstrate that hydrogenotrophic microbial pathways such as methanogenesis, acetogenesis, and sulfate reduction can consume hydrogen, modify fluid chemistry, and alter pore-scale wettability [40,128,166]. However, these experiments typically span days to months, leaving unresolved how such processes evolve over decades of storage. As detailed in Section 3.1.1, biofilm-driven wettability alteration is consistently observed, although its direction is not uniform across studies, with reported shifts toward both reduced water-wetness that can enhance gas mobility and increased hydrophilicity depending on surface chemistry and biofilm composition [4,14,17,128]. The conditions under which these opposing outcomes dominate, and their persistence under cyclic injection-withdrawal, remain poorly understood. Moreover, although permeability reduction by biofilm clogging has been suggested [62], no long-term experiments have systematically quantified its influence on injectivity across cycles. Perhaps the least constrained domain is the coupling between biotic and abiotic reactions. Microbial sulfate reduction can precipitate FeS and modify porosity and permeability, while biofilm-driven pH shifts may accelerate carbonate dissolution. Although such interactions are acknowledged [84,161], their kinetics and implications for long-term storage integrity remain poorly quantified, as current numerical models treat these reactions as separable processes, overlooking synergistic pathways that may amplify hydrogen loss or alter reservoir properties.

Overall, these uncertainties demonstrate that UHS is governed by strongly coupled, time-dependent, and scale-dependent processes that violate many simplifying assumptions embedded in current experimental protocols and reservoir simulators. Wettability evolves dynamically, displacement is rate sensitive and intermittent, trapping is history dependent, gas redistribution occurs over diffusive timescales, and biogeochemical feedback alters both pore structure and fluid properties. Addressing these challenges requires coordinated experimental programs integrating pore-scale imaging, long-duration core floods, multicomponent reactive transport modelling, and cyclic flow protocols under reservoir-representative conditions. Without such cross-scale integration, predictive upscaling of hydrogen storage performance will remain fundamentally uncertain.

5. Concluding remarks

This review consolidates the current understanding of underground hydrogen storage as a long-duration energy storage solution capable of supporting low-carbon-dominated energy systems, examines whether existing frameworks are adequate to describe its governing processes, and identifies critical directions for advancing its scientific and technical maturity. By synthesizing studies across pore, core, and reservoir scales, we show that UHS performance in porous media is governed by a tightly coupled interaction of multiphase flow dynamics, geochemical reactions, and microbial processes whose relative dominance shifts with lithology, brine composition, and operating regime.

Laboratory and pore-scale measurements have established a defensible baseline for hydrogen-brine flow behaviour. Reported endpoint hydrogen relative permeabilities fall within $k_{r,H_2} \approx 0.003\text{--}0.083$, roughly an order of magnitude below CO_2 -brine endpoints on comparable lithologies, and the fitted Brooks-Corey gas-phase exponents span $n_g \approx 3\text{--}10$, well above the $n_g \approx 1.6\text{--}1.8$ typical of supercritical CO_2 -brine on Berea Sandstones. Hydrogen-rock wettability is not uniformly strongly water-wet, and varies systematically with mineralogy, surface chemistry, and brine composition, ranging from strongly water-wet on pristine rocks to intermediate- or even gas-wet under organic ageing, hydrocarbon contact, or biofilm alteration. The Flow Zone Indicator framework was introduced to capture variability in hydrogen trapping behaviour, attributing much of the inter-study scatter in trapping efficiency to differences in pore-network architecture. It further suggests that high- FZI rocks favour deliverability while low- FZI flow units favour storage security.

Beyond this static baseline, UHS performance is shaped by dynamic and non-equilibrium processes that are not fully captured in current studies. Hydrogen combines an unfavourable mobility ratio with a high gravity number, a coupling that is uncommon among storage gases and that underpins viscous fingering, gravity override, and the reduced sweep efficiency reported in displacement experiments. Cyclic injection-withdrawal, intrinsic to UHS but largely absent in CO_2 geo-sequestration, alters interfacial and transport properties over repeated cycles, and the time-domain framing of cyclic operation, expressed through dynamic dimensionless groups, remains largely absent from the literature. At the pore scale, displacement is dominated by capillary forces at low capillary number with frequent snap-off and ganglion fragmentation, while transient bursts and Haines-jump pressure oscillations show that the displacement front is intermittent rather than smoothly advancing. As injection rates increase, displacement transitions toward viscous-dominated regimes, producing intermittent flow that strongly influences sweep efficiency and recovery dynamics. These flow regimes highlight the dependence of hydrogen migration and trapping on pore structure, wettability, and injection conditions. The strong variability of these parameters across lithologies underscores that UHS performance cannot be generalized across reservoir types or operational strategies.

Despite rapid progress, hysteresis under cyclic injection-withdrawal is poorly constrained, with reported recoverable fractions falling to 16–25% once hysteresis is accounted for and divergent evidence on whether residual hydrogen stabilizes after a few cycles or accumulates progressively over long storage times. Time-dependent wettability alteration driven by brine chemistry, microbial activity, and secondary mineral formation remains inadequately quantified, as do coupled geochemical-geomechanical effects on porosity evolution, caprock integrity, and wellbore performance. Most published datasets focus on pure hydrogen systems, whereas practical UHS operations often involve multi-component gas mixtures whose dissolution, diffusion, and redistribution further complicate trapping and recovery. The reliability of available datasets varies with method, with steady-state co-injection equilibrated at each fractional flow providing more defensible relative-permeability curves than unsteady-state inverse analyses that are vulnerable to channelized-flow artefacts, and with imaging-corroborated trapping measurements more defensible than those inferred from pressure data alone.

Advancing UHS toward reliable field deployment therefore requires coordinated, cross-scale research strategies. Priority should be given to four areas. The first is long-duration laboratory experiments that explicitly reproduce cyclic injection-withdrawal under representative pressure, temperature, and geochemical conditions, including mixed cushion-gas systems and cyclic effective-stress loading. The second is integrated imaging approaches that resolve transient pore-scale dynamics and address hydrogen's contrast through dopants, dual-energy acquisition, or surrogate gases. The third is multicomponent reactive transport models that couple flow, chemistry, biology, and geomechanics across scales and represent the time-domain scaling of cyclic

operation explicitly. The fourth is standardized side-by-side benchmarking on identical lithologies under identical protocols, with consistent reporting of measurement stage and saturation history, which is essential to resolve the inter-study contradictions noted throughout this review. While UHS has clear potential to enable large-scale renewable energy integration, realizing this potential depends on moving beyond static, generalized descriptions toward predictive frameworks that capture the coupled, time-dependent, and lithology-dependent nature of hydrogen storage in the subsurface. These developments will enable the design of safer, more efficient, and more predictable hydrogen storage systems that support large-scale low-carbon energy deployment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data for this article can be found online at doi:10.1016/j.rser.2026.117287.

Data availability

Data will be made available upon request.

References

- [1] Abdellatif M, Hashemi M, Azizmohammadi S. Large-scale underground hydrogen storage: integrated modeling of reservoir-wellbore system. *Int J Hydrog Energy* 2023;48:19160–71. <https://doi.org/10.1016/j.ijhydene.2023.01.227>
- [2] AbuAisha M, Billiotte J. A discussion on hydrogen migration in rock salt for tight underground storage with an insight into a laboratory setup. *J Energy Storage* 2021;38:102589. <https://doi.org/10.1016/j.est.2021.102589>
- [3] Aftab A, Al-Yaseri A, Nzila A, Al Hamad J, Amao AO, Sarmadivaleh M. Quartz-H₂-brine bacterium wettability under realistic geo-conditions: towards geological hydrogen storage. *Energy Fuels* 2023;37:5623–31. <https://doi.org/10.1021/acs.energyfuels.3c00163>
- [4] Aftab A, Al-Yaseri A, Nzila A, Hamad JA, Sarmadivaleh M. Microbial impact on basalt-water-hydrogen system: insights into wettability, capillary pressure, and interfacial tension for subsurface hydrogen storage. *Greenh Gases Sci Technol* 2024;14:546–60. <https://doi.org/10.1002/ghg.2277>
- [5] Al-Mukainah H, Al-Yaseri A, Yekeen N, Al Hamad J, Mahmoud M. Wettability of shale-brine-H₂ system and H₂-brine interfacial tension for assessment of the sealing capacities of shale formations during underground hydrogen storage. *Energy Rep* 2022;8:8830–43. <https://doi.org/10.1016/j.egy.2022.07.004>
- [6] Al-Yaseri A, Amao A, Fatah A. Experimental investigation of shale/hydrogen geochemical interactions. *Fuel* 2023;346:128272. <https://doi.org/10.1016/j.fuel.2023.128272>
- [7] Al-Yaseri A, Esteban L, Giwelli A, Abdel-Azeim S, Sarout J, Sarmadivaleh M. Impact of wettability on storage and recovery of hydrogen gas in the lesueur sandstone formation (southwest hub project, Western Australia). *Int J Hydrog Energy* 2023;48:23581–93. <https://doi.org/10.1016/j.ijhydene.2023.03.131>
- [8] Al-Yaseri A, Esteban L, Giwelli A, Sarout J, Lebedev M, Sarmadivaleh M. Initial and residual trapping of hydrogen and nitrogen in Fontainebleau sandstone using nuclear magnetic resonance core flooding. *Int J Hydrog Energy* 2022;47:22482–94. <https://doi.org/10.1016/j.ijhydene.2022.05.059>
- [9] Al-Yaseri A, Esteban L, Yekeen N, Giwelli A, Sarout J, Sarmadivaleh M. The effect of clay on initial and residual saturation of hydrogen in clay-rich sandstone formation: implications for underground hydrogen storage. *Int J Hydrog Energy* 2023;48:5175–85. <https://doi.org/10.1016/j.ijhydene.2022.11.059>
- [10] Al-Yaseri A, Fatah A. Impact of H₂-CH₄ mixture on pore structure of sandstone and limestone formations relevant to subsurface hydrogen storage. *Fuel* 2024;358:130192. <https://doi.org/10.1016/j.fuel.2023.130192>
- [11] Al-Yaseri A, Fatah A, Alsaif B, Sakthivel S, Amao A, Al-Qasim AS, Yousef AA. Subsurface hydrogen storage in limestone rocks: evaluation of geochemical reactions and gas generation potential. *Energy Fuels* 2024;38:9923–32. <https://doi.org/10.1021/acs.energyfuels.4c00742>
- [12] Al-Yaseri A, Fatah A, Amao A, Wolff-Boenisch D. Basalt-hydrogen-water interactions at geo-storage conditions. *Energy Fuels* 2023;37:15138–52. <https://doi.org/10.1021/acs.energyfuels.3c02502>
- [13] Al-Yaseri A, Hussaini SR, Fatah A, Al-Qasim AS, Patil PD. Computerized tomography analysis of potential geochemical reactions of carbonate rocks during underground hydrogen storage. *Fuel* 2024;361:130680. <https://doi.org/10.1016/j.fuel.2023.130680>
- [14] Al-Yaseri A, Sakthivel S, Yekeen N, Norrman K, Nzila A. The influence of microbial activities on the capillary pressure during H₂ injection: implications for underground H₂ storage. *Energy Fuels* 2024;38:499–505. <https://doi.org/10.1021/acs.energyfuels.3c03640>
- [15] Al-Yaseri A, Yekeen N, Al-Mukainah H, Hassanpouryouzband A. Geochemical interactions in geological hydrogen storage: the role of sandstone clay content. *Fuel* 2024;361:130728. <https://doi.org/10.1016/j.fuel.2023.130728>
- [16] Aldhuhoori M, Belhaj H, Alhameli F, Aljaberi F. Abiotic evaluation of geochemical reactions of sandstone minerals and their impact on underground hydrogen storage. *Int J Hydrog Energy* 2025;109:927–44. <https://doi.org/10.1016/j.ijhydene.2025.02.106>
- [17] Ali M, Arif M, Sedev R, Sánchez-Román M, Keshavarz A, Iglauer S. Underground hydrogen storage: the microbiotic influence on rock wettability. *J Energy Storage* 2023;72:108405. <https://doi.org/10.1016/j.est.2023.108405>
- [18] Ali M, Jha NK, Al-Yaseri A, Zhang Y, Iglauer S, Sarmadivaleh M. Hydrogen wettability of quartz substrates exposed to organic acids; implications for hydrogen geo-storage in sandstone reservoirs. *J Pet Sci Eng* 2021;207:109081. <https://doi.org/10.1016/j.petrol.2021.109081>
- [19] Ali M, Pan B, Yekeen N, Al-Ansari S, Al-Anazi A, Keshavarz A, Iglauer S, Hoteit H. Assessment of wettability and rock-fluid interfacial tension of caprock: implications for hydrogen and carbon dioxide geo-storage. *Int J Hydrog Energy* 2022;47:14104–20. <https://doi.org/10.1016/j.ijhydene.2022.02.149>
- [20] Alms K, Ahrens B, Graf M, Nehler M. Linking geological and infrastructural requirements for large-scale underground hydrogen storage in Germany. *Front Energy Res* 2023;11. <https://doi.org/10.3389/fenrg.2023.1172003>
- [21] AlOmier A, Hoecherl M, Cha D, Ayrala S, Yousef AA, Hoteit H. Experimental investigation of the impact of mixed wettability on pore-scale fluid displacement: a microfluidic study. *ACS Appl Mater Interfaces* 2024;16:69165–79. <https://doi.org/10.1021/acsami.4c13018>
- [22] AlZaabi A, Alzahrani HM, Alhosani A, Bijeljic B, Blunt MJ. Wettability, pore occupancy, connectivity and ostwald ripening of nitrogen, carbon dioxide, and hydrogen in carbonate rocks: a comparative study. *Int J Hydrog Energy* 2025;135:596–608. <https://doi.org/10.1016/j.ijhydene.2025.04.399>
- [23] Amrollahinasab O, Jammerneegg B, Azizmohammadi S, Ott H. On the interpretation of unsteady state experiments in heterogeneous rock by stochastic methods. *InterPore J* 2025;2. <https://doi.org/10.69631/ijp.v2i2n44>
- [24] Arif M, Al-Yaseri AZ, Barifcani A, Lebedev M, Iglauer S. Impact of pressure and temperature on CO₂-brine-mica contact angles and CO₂-brine interfacial tension: implications for carbon geo-sequestration. *J Colloid Interface Sci* 2016;462:208–15. <https://doi.org/10.1016/j.jcis.2015.09.076>
- [25] Arif M, Lebedev M, Barifcani A, Iglauer S. CO₂ storage in carbonates: wettability of calcite. *Int J Greenh Gas Control* 2017;62:113–21. <https://doi.org/10.1016/j.jggc.2017.04.014>
- [26] Aslannezhad M, Ali M, Kalantariasl A, Sayyafzadeh M, You Z, Iglauer S, Keshavarz A. A review of hydrogen/rock/brine interaction: implications for hydrogen geo-storage. *Prog Energy Combust Sci* 2023;95:101066. <https://doi.org/10.1016/j.peccs.2022.101066>
- [27] Astsaury T, Habiburrahman M, Ibrahim AF, Wang Y. Utilizing machine learning for flow zone indicators prediction and hydraulic flow unit classification. *Sci Rep* 2024;14:4223. <https://doi.org/10.1038/s41598-024-54893-1>
- [28] Awolayo A, Sarma H, AlSumaiti A. An experimental investigation into the impact of sulfate ions in smart water to improve oil recovery in carbonate reservoirs. *Transp Porous Media* 2016;111:649–68. <https://doi.org/10.1007/s11242-015-0616-4>
- [29] Awolayo AN, Sarma HK, Nghiem LX. Thermodynamic modeling of brine dilution-dependent recovery in carbonate rocks with different mineralogical content. *Energy Fuels* 2018;32:8921–43. <https://doi.org/10.1021/acs.energyfuels.8b01080>
- [30] Bachu S. Drainage and imbibition CO₂/brine relative permeability curves at in situ conditions for sandstone formations in Western Canada. *Energy Procedia* 2013;37:4428–36. <https://doi.org/10.1016/j.egypro.2013.07.001>
- [31] Bagheri M, Mahani H, Ayatollahi S, Zivar D. Direct pore-scale simulation of the effect of capillary number and gas compressibility on cyclic underground hydrogen storage & production in heterogeneous aquifers. *Adv Water Resour* 2023;181:104547. <https://doi.org/10.1016/j.advwatres.2023.104547>
- [32] Bahrami M, Mahani H, Zivar D, Ayatollahi S. Microfluidic investigation of pore-scale flow behavior and hysteresis in underground hydrogen storage in sandstones. *J Energy Storage* 2024;98:112959. <https://doi.org/10.1016/j.est.2024.112959>
- [33] Bennion DB, Bachu S. Drainage and imbibition relative permeability relationships for supercritical CO₂/brine and H₂S/brine systems in intergranular sandstone, carbonate, shale, and anhydrite rocks. *SPE Reserv Eval Eng* 2008;11:487–96. <https://doi.org/10.2118/99326-PA>
- [34] Bensing JP, Misch D, Skerbisich L, Sachsenhofer RF. Hydrogen-induced calcite dissolution in amalthenton formation claystones: implications for underground hydrogen storage caprock integrity. *Int J Hydrog Energy* 2022;47:30621–6. <https://doi.org/10.1016/j.ijhydene.2022.07.023>

- [35] Bhaduriya V, Kaur J, Sapale P, Rasane P, Singh J. Hydrogen storage in porous media: understanding and mitigating microbial risks for a sustainable future. *Int J Hydrog Energy* 2024;67:681–93. <https://doi.org/10.1016/j.ijhydene.2024.04.178>
- [36] Bijay KC, Frash LP, Creasy NM, Neil CW, Purswani P, Li W, Meng M, Iyare U, Gross MR. Laboratory study of cyclic underground hydrogen storage in porous media with evidence of a dry near-well zone and evaporation induced salt precipitation. *Int J Hydrog Energy* 2024;71:515–27. <https://doi.org/10.1016/j.ijhydene.2024.05.234>
- [37] Blunt MJ. *Multiphase flow in permeable media: a pore-scale perspective*. Cambridge, England: Cambridge University Press; 2017.
- [38] Blunt MJ. Ostwald ripening and gravitational equilibrium: implications for long-term subsurface gas storage. *Phys Rev E* 2022;106:045103. <https://doi.org/10.1103/PhysRevE.106.045103>
- [39] Bo Z, Hörning S, Underschultz JR, Garnett A, Hurter S. Effects of geological heterogeneity on gas mixing during underground hydrogen storage (uhs) in braided-fluvial reservoirs. *Fuel* 2024;357:129949. <https://doi.org/10.1016/j.fuel.2023.129949>
- [40] Boon M, Buntic I, Ahmed K, Dopffel N, Peters C, Hajibeygi H. Microbial induced wettability alteration with implications for underground hydrogen storage. *Sci Rep* 2024;14:8248. <https://doi.org/10.1038/s41598-024-58951-6>
- [41] Boon M, Hajibeygi H. Experimental characterization of H₂/water multiphase flow in heterogeneous sandstone rock at the core scale relevant for underground hydrogen storage (UHS). *Sci Rep* 2022;12:14604. <https://doi.org/10.1038/s41598-022-18759-8>
- [42] Boon M, Rademaker T, Winardhi CW, Hajibeygi H. Multiscale experimental study of H[formula: see text]/brine multiphase flow in porous rock characterizing relative permeability hysteresis, hydrogen dissolution, and ostwald ripening. *Sci Rep* 2024;14:30170. <https://doi.org/10.1038/s41598-024-81720-4>
- [43] Braid H, Taylor K, Hough E, Rochelle C, Niasar V, Ma L. Hydrogen-induced mineral alteration: a review in the context of underground hydrogen storage (uhs) in saline aquifers. *Earth-Sci Rev* 2024;259:104975. <https://doi.org/10.1016/j.earscirev.2024.104975>
- [44] Burnside NM, Naylor M. Review and implications of relative permeability of CO₂/brine systems and residual trapping of CO₂. *Int J Greenh Gas Control* 2014;23:1–11. <https://doi.org/10.1016/j.jggc.2014.01.013>
- [45] de Chalendar JA, Garing C, Benson SM. Pore-scale modelling of ostwald ripening. *J Fluid Mech* 2018;835:363–92. <https://doi.org/10.1017/jfm.2017.720>
- [46] Chaturvedi KR, Bajpai S, Trivedi J, Sharma T. Air foams for mobility control and subsurface storage of hydrogen in porous media: an experimental study. *Energy Fuels* 2022;36:5036–46. <https://doi.org/10.1021/acs.energyfuels.1c04246>
- [47] Chen F, Chen B, Mao S, Malki M, Mehana M. Integrating capacity and efficiency for optimal hydrogen storage site selection in saline aquifers. *Energy Fuels* 2024;38:4733–42. <https://doi.org/10.1021/acs.energyfuels.3c04852>
- [48] Chen X, Gao S, Kianinejad A, DiCarlo DA. Steady-state supercritical CO₂ and brine relative permeability in Berea sandstone at different temperature and pressure conditions: SC-CO₂ and brine reperm in Berea. *Water Resour Res* 2017;53:6312–21. <https://doi.org/10.1002/2017WR020810>
- [49] Cheng C, Busch B, Kontny A, Hilgers C. Underground hydrogen storage in sandstone reservoirs: effects of geochemical reactivity of hydrogen on reservoir performance. *Int J Hydrog Energy* 2025;105:492–504. <https://doi.org/10.1016/j.ijhydene.2025.01.330>
- [50] Chow YTF, Maitland GC, Trusler JPM. Interfacial tensions of (H₂O + H₂) and (H₂O + CO₂ + H₂) systems at temperatures of (298–448) K and pressures up to 45 MPa. *Fluid Ph Equilibria* 2018;475:37–44. <https://doi.org/10.1016/j.fluid.2018.07.022>
- [51] Dabbaghi E, Ng K, Brown TC, Yu Y. Experimental study on the effect of hydrogen on the mechanical properties of hulett sandstone. *Int J Hydrog Energy* 2024;60:468–78. <https://doi.org/10.1016/j.ijhydene.2024.02.210>
- [52] Dalton LE, Tapriyal D, Crandall D, Goodman A, Shi F, Haeri F. Contact angle measurements using sessile drop and micro-CT data from six sandstones. *Transp Porous Media* 2020;133:71–83. <https://doi.org/10.1007/s11242-020-01415-y>
- [53] Davies K, Esteban L, Sarout J, Keshavarz A, Iglauer S. Hydrogen-induced transformations in dolomite: unlocking natural hydrogen exploration and subsurface storage in carbonates. *Energy Fuels* 2025;39:6644–53. <https://doi.org/10.1021/acs.energyfuels.5c00322>
- [54] Dehghani MR, Ghazi SF, Kazemzadeh Y. Interfacial tension and wettability alteration during hydrogen and carbon dioxide storage in depleted gas reservoirs. *Sci Rep* 2024;14:11594. <https://doi.org/10.1038/s41598-024-62458-5>
- [55] Dehury R, Chowdhury S, Sangwai JS. Dynamics of hydrogen storage in subsurface saline aquifers: a computational and experimental pore-scale displacement study. *Int J Hydrog Energy* 2024;69:817–36. <https://doi.org/10.1016/j.ijhydene.2024.05.009>
- [56] Dilshan RADP, Perera MSA. The impact of acetic acid reaction on microstructural and mineralogical changes in shale caprock: a preliminary study for underground hydrogen storage integrity. *Int J Hydrog Energy* 2025;166:150900. <https://doi.org/10.1016/j.ijhydene.2025.150900>
- [57] Dodangoda C, Haque A, Zeng L, Yang SQ, Ranjith PG. Underground hydrogen storage: insights into hydrogen reactivity and porosity dynamics for optimizing clean energy storage in depleted reservoirs. *Renew Energy* 2025;251:123357. <https://doi.org/10.1016/j.renene.2025.123357>
- [58] Dohrmann AB, Krüger M. Microbial H₂ consumption by a formation fluid from a natural gas field at high-pressure conditions relevant for underground H₂ storage. *Environ Sci Technol* 2023;57:1092–102. <https://doi.org/10.1021/acs.est.2c07303>
- [59] Dokhon W, AlZaabi A, Bijeljic B, Blunt MJ. Micro-CT imaging of drainage and spontaneous imbibition for underground hydrogen storage in saline aquifers. *Adv Water Resour* 2025;204:105064. <https://doi.org/10.1016/j.advwatres.2025.105064>
- [60] Dokhon W, Goodarzi S, Alzahrani HM, Blunt MJ, Bijeljic B. Pressure decline and gas expansion in underground hydrogen storage: a pore-scale percolation study. *Int J Hydrog Energy* 2024;86:261–74. <https://doi.org/10.1016/j.ijhydene.2024.08.139>
- [61] Dong Z, Wang D, Yang S, Yang M, Li Y, Du D. Mechanism exploration of the hydrodynamic trapping of hydrogen in geological formations via the pore-scale numerical studies. *Int J Hydrog Energy* 2025;159:150509. <https://doi.org/10.1016/j.ijhydene.2025.150509>
- [62] Dopffel N, Jansen S, Gerritse J. Microbial side effects of underground hydrogen storage—knowledge gaps, risks and opportunities for successful implementation. *Int J Hydrog Energy* 2021;46:8594–606. <https://doi.org/10.1016/j.ijhydene.2020.12.058>
- [63] Dopffel N, Mayers K, Kadir A, Alagic E, An-Stepec BA, Djurhuus K, Boldt D, Beeder J, Hoth S. Microbial hydrogen consumption leads to a significant pH increase under high-saline-conditions: implications for hydrogen storage in salt caverns. *Sci Rep* 2023;13:10564. <https://doi.org/10.1038/s41598-023-37630-y>
- [64] Dopffel N, Mayers K, Kadir A, An-Stepec BA, Beeder J, Hoth S. Exploring microbiological dynamics in a salt cavern for potential hydrogen storage use. *Environ Microbiol Rep* 2025;17:e70064. <https://doi.org/10.1111/1758-2229.70064>
- [65] Erfani Gahrooei HR, Ghazanfari MH, Karimi Malekabadi F. Wettability alteration of reservoir rocks to gas wetting condition: a comparative study. *Can J Chem Eng* 2018;96:997–1004. <https://doi.org/10.1002/cjce.23023>
- [66] Ershadnia R, Singh M, Mahmoodpour S, Meyal A, Moeni F, Hosseini SA, Sturmer DM, Rasoulzadeh M, Dai Z, Soltanian MR. Impact of geological and operational conditions on underground hydrogen storage. *Int J Hydrog Energy* 2023;48:1450–71. <https://doi.org/10.1016/j.ijhydene.2022.09.208>
- [67] Esfandiyari H, Sarmadivaleh M, Esmaeilzadeh F, Ali M, Iglauer S, Keshavarz A. Experimental evaluation of rock mineralogy on hydrogen-wettability: implications for hydrogen geo-storage. *J Energy Storage* 2022;52:104866. <https://doi.org/10.1016/j.est.2022.104866>
- [68] Fatah A, Al Ramadan M, Al-Yaseri A. Hydrogen impact on cement integrity during underground hydrogen storage: a minireview and future outlook. *Energy Fuels* 2024;38:1713–28. <https://doi.org/10.1021/acs.energyfuels.3c04364>
- [69] Fatah A, Al-Yaseri A. Geomechanical integrity and geochemical reactions of shale caprocks for hydrogen storage: a comprehensive review. *Fuel* 2025;400:135728. <https://doi.org/10.1016/j.fuel.2025.135728>
- [70] Fatah A, Al-Yaseri A. Petrophysical impacts of CO₂ as cushion gas in subsurface hydrogen storage. *Energy Fuels* 2025;39:6892–904. <https://doi.org/10.1021/acs.energyfuels.4c06132>
- [71] Fatah A, Al-Yaseri A, Alshammari S, Al-Qasim AS. Gas injection dynamics and hydrogen storage in carbonate reservoirs: core-flooding and molecular simulation study. *Energy Fuels* 2024;38:20951–66. <https://doi.org/10.1021/acs.energyfuels.4c03699>
- [72] Fatah A, Al-Yaseri A, Radwan OA, Theravalappil R. Clay minerals and hydrogen: insights into reactivity, pore structure, and chemical stability. *Fuel* 2025;389:134615. <https://doi.org/10.1016/j.fuel.2025.134615>
- [73] Flesch S, Pudlo D, Albrecht D, Jacob A, Enzmann F. Hydrogen underground storage—petrographic and petrophysical variations in reservoir sandstones from laboratory experiments under simulated reservoir conditions. *Int J Hydrog Energy* 2018;43:20822–35. <https://doi.org/10.1016/j.ijhydene.2018.09.112>
- [74] Foroughi S, Shojaei MJ, Lane N, Rashid B, Lakshatanov D, Ning Y, Zapata Y, Bijeljic B, Blunt MJ. A framework for multiphase pore-scale modeling based on micro-CT imaging. *Transp Porous Media* 2025;152. <https://doi.org/10.1007/s11242-025-02156-6>
- [75] Galvis-Silva H, Okoroafor ER. Investigating rock alterations in underground hydrogen storage: a geochemical and geomechanical baseline study. *J Energy Storage* 2024;101:113939. <https://doi.org/10.1016/j.est.2024.113939>
- [76] Gao J, Kong D, Peng Y, Zhou Y, Liu Y, Zhu W. Pore-scale mechanisms and hysteresis effect during multi-cycle injection and production process in underground hydrogen storage reservoir. *Energy (Oxf.)* 2023;283:129007. <https://doi.org/10.1016/j.energy.2023.129007>
- [77] Garing C, de Chalendar JA, Voltolini M, Ajo-Franklin JB, Benson SM. Pore-scale capillary pressure analysis using multi-scale X-ray micromotography. *Adv Water Resour* 2017;104:223–41. <https://doi.org/10.1016/j.advwatres.2017.04.006>
- [78] Gelencsér O, Árvai C, Mika LT, Breiter D, LeClair D, Szabó C, Falus G, Szabó-Krausz Z. Effect of hydrogen on calcite reactivity in sandstone reservoirs: experimental results compared to geochemical modeling predictions. *J Energy Storage* 2023;61:106737. <https://doi.org/10.1016/j.est.2023.106737>
- [79] Gholami R. Hydrogen storage in geological porous media: solubility, mineral trapping, H₂S generation and salt precipitation. *J Energy Storage* 2023;59:106576. <https://doi.org/10.1016/j.est.2022.106576>
- [80] Gomez Mendez I, El-Sayed WMM, Menefee AH, Karpyn ZT. Insights into underground hydrogen storage challenges: a review on hydrodynamic and biogeochemical experiments in porous media. *Energy Fuels* 2024;38:20015–32. <https://doi.org/10.1021/acs.energyfuels.4c03142>
- [81] Goodarzi S, Zhang G, Bijeljic B, Blunt MJ. Ostwald ripening leads to less hysteresis during hydrogen injection and withdrawal: a pore-scale imaging study. *Int J Hydrog Energy* 2025;114:475–85. <https://doi.org/10.1016/j.ijhydene.2025.02.066>
- [82] Goodarzi S, Zhang Y, Foroughi S, Bijeljic B, Blunt MJ. Trapping, hysteresis and ostwald ripening in hydrogen storage: a pore-scale imaging study. *Int J Hydrog Energy* 2024;56:1139–51. <https://doi.org/10.1016/j.ijhydene.2023.12.029>
- [83] Guo R, Ershadnia R, Wang H, Hosseini SA, Zhao Q. Microfluidic experiments on hydrogen behavior in heterogeneous rocks during underground hydrogen storage in saline aquifers. *Fuel* 2025;391:134731. <https://doi.org/10.1016/j.fuel.2025.134731>

- [84] Haddad PG, Ranchou-Peyruse M, Guignard M, Mura J, Casteran F, Ronjon-Magand L, Senechal P, Isaure MP, Moonen P, Hoareau G, Dequidt D, Chiquet P, Caumette G, Cezac P, Ranchou-Peyruse A. Geological storage of hydrogen in deep aquifers—an experimental multidisciplinary study. *Energy Environ Sci* 2022;15:3400–15. <https://doi.org/10.1039/d2ee00765g>
- [85] Hashemi L, Blunt M, Hajibeygi H. Pore-scale modelling and sensitivity analyses of hydrogen-brine multiphase flow in geological porous media. *Sci Rep* 2021;11:8348. <https://doi.org/10.1038/s41598-021-87490-7>
- [86] Hashemi L, Glerum W, Farajzadeh R, Hajibeygi H. Contact angle measurement for hydrogen/brine/sandstone system using captive-bubble method relevant for underground hydrogen storage. *Adv Water Resour* 2021;154:103964. <https://doi.org/10.1016/j.advwatres.2021.103964>
- [87] Hashemi L, Vuik C. Critical assessment of the validity of quasi-static pore network modeling in the application of underground hydrogen storage. *Adv Water Resour* 2024;193:104812. <https://doi.org/10.1016/j.advwatres.2024.104812>
- [88] Hashemi M, Sedaee B. Understanding caprock integrity in underground hydrogen storage: a geochemical study of mineral alteration and sealing efficiency. *Int J Hydrog Energy* 2025;154:150300. <https://doi.org/10.1016/j.ijhydene.2025.150300>
- [89] Hassanpouryouzband A, Adie K, Cowen T, Thaysen EM, Heinemann N, Butler IB, Wilkinson M, Edlmann K. Geological hydrogen storage: geochemical reactivity of hydrogen with sandstone reservoirs. *ACS Energy Lett* 2022;7:2203–10. <https://doi.org/10.1021/acsenergylett.2c01024>
- [90] He X, Wang Y, Zheng Y, Zhang W, Dai Y, Zou H. Pore-scale gas–water two-phase flow mechanisms for underground hydrogen storage: a mini review of theory, experiment, and simulation. *Appl. Sci. (Basel)* 2025;15:5657. <https://doi.org/10.3390/app15105657>
- [91] Heinemann N, Alcalde J, Miocic JM, Hangx SJT, Kallmeyer J, Ostertag-Henning C, Hassanpouryouzband A, Thaysen EM, Strobel GJ, Schmidt-Hattenberger C, Edlmann K, Wilkinson M, Bentham M, Stuart Haszeldine R, Carbonell R, Rudloff A. Enabling large-scale hydrogen storage in porous media—the scientific challenges. *Energy Environ Sci* 2021;14:853–64. <https://doi.org/10.1039/d0ee03536j>
- [92] Hellerschmid C, Schritter J, Waldmann N, Zaduryan AB, Rachbauer L, Scherr KE, Andiappan A, Bauer S, Pichler M, Loibner AP. Hydrogen storage and geo-methanation in a depleted underground hydrocarbon reservoir. *Nat Energy* 2024;9:333–44. <https://doi.org/10.1038/s41560-024-01458-1>
- [93] Hematpur H, Abdollahi R, Rostami S, Haghighi M, Blunt MJ. Review of underground hydrogen storage: concepts and challenges. *Adv Geo-Energy Res* 2023;7:111–31. <https://doi.org/10.46690/ager.2023.02.05>
- [94] Hemmati N, Borazjani S, Badalyan A, Genolet L, Behr A, Zeinijahromi A, Bedrikovetsky P. Determining relative permeability and capillary pressure from mixed-wet core floods. *Geoenviron Sci Eng* 2024;239:212885. <https://doi.org/10.1016/j.geoen.2024.212885>
- [95] Herring AL, Andersson L, Wildenschild D. Enhancing residual trapping of supercritical CO₂ via cyclic injections. *Geophys Res Lett* 2016;43:9677–85. <https://doi.org/10.1002/2016gl070304>
- [96] Higgs S, Da Wang Y, Sun C, Ennis-King J, Jackson S, Armstrong R, Mostaghimi P. In-situ hydrogen wettability characterisation for underground hydrogen storage. *EarthArXiv* 2021;13062–75. <https://doi.org/10.31223/x54045>
- [97] Higgs S, Da Wang Y, Sun C, Ennis-King J, Jackson SJ, Armstrong RT, Mostaghimi P. Comparative analysis of hydrogen, methane and nitrogen relative permeability: implications for underground hydrogen storage. *J Energy Storage* 2023;73:108827. <https://doi.org/10.1016/j.est.2023.108827>
- [98] Higgs S, Wang YD, Sun C, Ennis-King J, Jackson SJ, Armstrong RT, Mostaghimi P. Direct measurement of hydrogen relative permeability hysteresis for underground hydrogen storage. *Int J Hydrog Energy* 2024;50:524–41. <https://doi.org/10.1016/j.ijhydene.2023.07.270>
- [99] Hosseini M, Ali M, Fahimpour J, Keshavarz A, Iglauer S. Assessment of rock-hydrogen and rock-water interfacial tension in shale, evaporite and basaltic rocks. *J Nat Gas Sci Eng* 2022;106:104743. <https://doi.org/10.1016/j.jngse.2022.104743>
- [100] Hosseini M, Ali M, Fahimpour J, Keshavarz A, Iglauer S. Basalt-H₂-brine wettability at geo-storage conditions: implication for hydrogen storage in basaltic formations. *J Energy Storage* 2022;52:104745. <https://doi.org/10.1016/j.est.2022.104745>
- [101] Hosseini M, Ali M, Fahimpour J, Keshavarz A, Iglauer S. Calcite–fluid interfacial tension: H₂ and CO₂ geological storage in carbonates. *Energy Fuels* 2023;37:5986–94. <https://doi.org/10.1021/acs.energyfuels.3c00399>
- [102] Hosseini M, Fahimpour J, Ali M, Keshavarz A, Iglauer S. H₂-brine interfacial tension as a function of salinity, temperature, and pressure; implications for hydrogen geo-storage. *J Pet Sci Eng* 2022;213:110441. <https://doi.org/10.1016/j.petrol.2022.110441>
- [103] Hosseini M, Fahimpour J, Ali M, Keshavarz A, Iglauer S. Hydrogen wettability of carbonate formations: implications for hydrogen geo-storage. *J Colloid Interface Sci* 2022;614:256–66. <https://doi.org/10.1016/j.jcis.2022.01.068>
- [104] Hosseini M, Sedev R, Ali M, Ali M, Fahimpour J, Keshavarz A, Iglauer S. Hydrogen-wettability alteration of Indiana limestone in the presence of organic acids and nanofluid. *Int J Hydrog Energy* 2023;48:35220–8. <https://doi.org/10.1016/j.ijhydene.2023.05.292>
- [105] Hu Y, Guo Y, Qing H, Hou Y. Study on influencing factors and mechanism of pore compressibility of tight sandstone reservoir—a case study of upper carboniferous in Ordos basin. *Front Earth Sci* 2023;10:1100951. <https://doi.org/10.3389/feart.2022.1100951>
- [106] Ibitogbe E, Awolayo AN. Pore-scale evaluation of hydrogen storage and recovery in basaltic formations. *Adv Water Resour* 2025;205, Not Available. <https://doi.org/10.1016/j.advwatres.2025.105068>
- [107] Iglauer S. Optimum geological storage depths for structural H₂ geo-storage. *J Pet Sci Eng* 2022;212:109498. <https://doi.org/10.1016/j.petrol.2021.109498>
- [108] Iglauer S, Ali M, Keshavarz A. Hydrogen wettability of sandstone reservoirs: implications for hydrogen geo-storage. *Geophys Res Lett* 2021;48. <https://doi.org/10.1029/2020GL090814>
- [109] Isfehiani ZD, Sheidaie A, Hosseini M, Fahimpour J, Iglauer S, Keshavarz A. Interfacial tensions of (brine + H₂ + CO₂) systems at gas geo-storage conditions. *J Mol Liq* 2023;374:121279. <https://doi.org/10.1016/j.molliq.2023.121279>
- [110] Jafari Raad SM, Leonenko Y, Hassanzadeh H. Hydrogen storage in saline aquifers: opportunities and challenges. *Renew Sustain Energy Rev* 2022;168:112846. <https://doi.org/10.1016/j.rser.2022.112846>
- [111] Jangda Z, Menke H, Busch A, Geiger S, Bultreys T, Lewis H, Singh K. Pore-scale visualization of hydrogen storage in a sandstone at subsurface pressure and temperature conditions: trapping, dissolution and wettability. *J Colloid Interface Sci* 2023;629:316–25. <https://doi.org/10.1016/j.jcis.2022.09.082>
- [112] Jha NK, Al-Yaseri A, Ghasemi M, Al-Bayati D, Lebedev M, Sarmadivaleh M. Pore scale investigation of hydrogen injection in sandstone via X-ray micro-tomography. *Int J Hydrog Energy* 2021;46:34822–9. <https://doi.org/10.1016/j.ijhydene.2021.08.042>
- [113] Jia C, Ren B, Sepehrnoori K, Delshad M, Liu B, Sun H, Yao J. Numerical studies of hydrogen buoyant flow in storage aquifers. *Fuel* 2023;349:128755. <https://doi.org/10.1016/j.fuel.2023.128755>
- [114] Kalam S, Abu-Khamsin SA, Kamal MS, Abbasi GR, Lashari N, Patil S, Abdurrahman M. A mini-review on underground hydrogen storage: production to field studies. *Energy Fuels* 2023;37:8128–41. <https://doi.org/10.1021/acs.energyfuels.3c00841>
- [115] Kanaani M, Sedaee B, Asadian-Pakfar M. Role of cushion gas on underground hydrogen storage in depleted oil reservoirs. *J Energy Storage* 2022;45:103783. <https://doi.org/10.1016/j.est.2021.103783>
- [116] Kashefi K, Pereira LMC, Chapoy A, Burgass R, Tohidi B. Measurement and modelling of interfacial tension in methane/water and methane/brine systems at reservoir conditions. *Fluid Ph Equilibria* 2016;409:301–11. <https://doi.org/10.1016/j.fluid.2015.09.050>
- [117] Kim H, Ding S, Bondarenko N, Willette DC, Salahshoor S, Makhnenko RY. Experimental approaches for characterization of water-hydrogen flow in reservoir rock. *J Energy Storage* 2025;114:115785. <https://doi.org/10.1016/j.est.2025.115785>
- [118] Kim KY, Oh J, Han WS, Park KG, Shinn YJ, Park E. Two-phase flow visualization under reservoir conditions for highly heterogeneous conglomerate rock: a core-scale study for geologic carbon storage. *Sci Rep* 2018;8:4869. <https://doi.org/10.1038/s41598-018-23224-6>
- [119] Krevor S, de Coninck H, Gasda SE, Ghaleigh NS, de Gooyert V, Hajibeygi H, Juanes R, Neufeld J, Roberts JJ, Swennenhuis F. Subsurface carbon dioxide and hydrogen storage for a sustainable energy future. *Nat Rev Earth Environ* 2023;4:102–18. <https://doi.org/10.1038/s43017-022-00376-8>
- [120] Krevor SCM, Pini R, Zuo L, Benson SM. Relative permeability and trapping of CO₂ and water in sandstone rocks at reservoir conditions: multiphase flow of CO₂ and water in sandstone rocks. *Water Resour Res* 2012;48:W02532. <https://doi.org/10.1029/2011WR010859>
- [121] Kumar KR, Honorio H, Chandra D, Lesueur M, Hajibeygi H. Comprehensive review of geomechanics of underground hydrogen storage in depleted reservoirs and Salt caverns. *J Energy Storage* 2023;73:108912. <https://doi.org/10.1016/j.est.2023.108912>
- [122] Kumbhat DS, Ebigo A. Effect of relative permeability hysteresis on plume dynamics, wellbore flow regime, and storage efficiency in underground hydrogen storage. *Int J Hydrog Energy* 2024;91:243–55. URL: <https://doi.org/10.1016/j.ijhydene.2024.09.403>. <https://www.sciencedirect.com/science/article/pii/S0360319924041296>
- [123] Lardhi M, Haq B, Al Shehri D. Experimental evaluation of 3-phase and 4-phase surface phenomena for hydrogen storage in depleted oil reservoirs. *Int J Hydrog Energy* 2025;148:149775. <https://doi.org/10.1016/j.ijhydene.2025.05.405>
- [124] Lev E, Boyce CM. Opportunities for characterizing geological flows using magnetic resonance imaging. *iScience* 2020;23:101534. <https://doi.org/10.1016/j.isci.2020.101534>
- [125] Li G, Yao J. Snap-off during imbibition in porous media: mechanisms, influencing factors, and impacts. *Eng* 2023;4:2896–925. <https://doi.org/10.3390/eng4040163>
- [126] Li J, Yang Y, Yao J. Investigating hydrogen storage in porous media of saline aquifers: a numerical study on wettability and pore structure impact. In: *Annual meeting conference on porous media*; 2024. p. 913–24.
- [127] Li Y, Cheng Z, Xie C, Du F, Zhao H, Yin X, Huang J. Hydrogen storage efficiency under the effects of viscous fingering and gravity. *Energy Fuels* 2025;39:13083–94. <https://doi.org/10.1021/acs.energyfuels.5c01766>
- [128] Liu N, Kovscek AR, Fernø MA, Dopffel N. Pore-scale study of microbial hydrogen consumption and wettability alteration during underground hydrogen storage. *Front Energy Res* 2023;11. <https://doi.org/10.3389/fenrg.2023.1124621>
- [129] Liu Y, Yang D, Cai Y. Numerical study on hydrogen-water flow in the microfluidic model for underground hydrogen storage in aquifers. *Int J Hydrog Energy* 2025;113:406–19. <https://doi.org/10.1016/j.ijhydene.2025.02.479>
- [130] Lysy M, Erslund G, Fernø M. Pore-scale dynamics for underground porous media hydrogen storage. *Adv Water Resour* 2022;163:104167. <https://doi.org/10.1016/j.advwatres.2022.104167>
- [131] Lysy M, Fernø MA, Erslund G. Effect of relative permeability hysteresis on reservoir simulation of underground hydrogen storage in an offshore aquifer. *J Energy Storage* 2023;64:107229. <https://doi.org/10.1016/j.jest.2023.107229>
- [132] Lysy M, Føyen T, Johannesen EB, Fernø M, Erslund G. Hydrogen relative permeability hysteresis in underground storage. *Geophys Res Lett* 2022;49:e2022GL100364. <https://doi.org/10.1029/2022gl100364>

- [133] Lysy M, Liu N, Landa-Marbán D, Ersland G, Fernø M. Impact of gas type on microfluidic drainage experiments and pore network modeling relevant for underground hydrogen storage. *J Energy Storage* 2024;87:111439. <https://doi.org/10.1016/j.est.2024.111439>
- [134] Lysy M, Liu N, Solstad CM, Fernø MA, Ersland G. Microfluidic hydrogen storage capacity and residual trapping during cyclic injections: implications for underground storage. *Int J Hydrog Energy* 2023;48:31294–304. <https://doi.org/10.1016/j.ijhydene.2023.04.253>
- [135] Marquez R, Bullon J, Forgiarini A, Salager JL. The oscillatory spinning drop technique. An innovative method to measure dilational interfacial rheological properties of brine-crude oil systems in the presence of asphaltenes. *Colloids Interfaces* 2021;5:42. <https://doi.org/10.3390/colloids5030042>
- [136] Mascini A, Boone M, Van Offenwert S, Wang S, Cnudde V, Bultreys T. Fluid invasion dynamics in porous media with complex wettability and connectivity. *Geophys Res Lett* 2021;48:e2021GL095185. <https://doi.org/10.1029/2021gl095185>
- [137] Medina OE, Gallego JF, Moncayo-Riascos I, Lysy M, Benjumea PN, Cortés FB, Franco CA. Salinity influence on underground hydrogen storage: insights from molecular dynamics and pore-scale analysis. *Int J Hydrog Energy* 2024;60:959–75. <https://doi.org/10.1016/j.ijhydene.2024.02.073>
- [138] Miocic J, Heinemann N, Edlmann K, Scaffidi J, Molaei F, Alcalde J. Underground hydrogen storage: a review. *Geol Soc Spec Publ* 2023;528:73–86. <https://doi.org/10.1144/sp528-2022-88>
- [139] Mirchi V, Dejam M, Alvarado V. Interfacial tension and contact angle measurements for hydrogen-methane mixtures/brine/oil-wet rocks at reservoir conditions. *Int J Hydrog Energy* 2022;47:34963–75. <https://doi.org/10.1016/j.ijhydene.2022.08.056>
- [140] Mirchi V, Dejam M, Alvarado V, Akbarabadi M. Effect of cushion gas on hydrogen/brine flow behavior in oil-wet rocks with application to hydrogen storage in depleted oil and gas reservoirs. *Energy Fuels* 2023;37:15231–43. <https://doi.org/10.1021/acs.energyfuels.3c02884>
- [141] Mirzaei-Païman A, Ghanbarian B. A new method for characterizing dynamic reservoir quality: implications for quality maps in reservoir simulation and rock type classification. *J Pet Sci Eng* 2022;218:111049. <https://doi.org/10.1016/j.petrol.2022.111049>
- [142] Muhammed NS, Haq B, Al Shehri D, Al-Ahmed A, Rahman MM, Zaman E. A review on underground hydrogen storage: insight into geological sites, influencing factors and future outlook. *Energy Rep* 2022;8:461–99. <https://doi.org/10.1016/j.egyr.2021.12.002>
- [143] Muhammed NS, Haq MB, Al Shehri DA, Al-Ahmed A, Rahman MM, Zaman E, Iglauer S. Hydrogen storage in depleted gas reservoirs: a comprehensive review. *Fuel* 2023;337:127032. <https://doi.org/10.1016/j.fuel.2022.127032>
- [144] Naquash A, Agarwal N, Lee M. A review on liquid hydrogen storage: current status, challenges and future directions. *Sustainability* 2024;16:8270. <https://doi.org/10.3390/su16188270>
- [145] Nazari M, Mahani H, Ayatollahi S. Pore-scale insights on mixed-wettability and its impact on underground hydrogen storage in aquifers. *Adv Water Resour* 2025;204. Not Available. <https://doi.org/10.1016/j.advwatres.2025.105044>
- [146] Neumann AW, Good RJ, Hope CJ, Seipal M. An equation-of-state approach to determine surface tensions of low-energy solids from contact angles. *J Colloid Interface Sci* 1974;49:291–304. [https://doi.org/10.1016/0021-9797\(74\)90365-8](https://doi.org/10.1016/0021-9797(74)90365-8)
- [147] Oliveira AM, Beswick RR, Yan Y. A green hydrogen economy for a renewable energy society. *Curr Opin Chem Eng* 2021;33:100701. <https://doi.org/10.1016/j.coche.2021.100701>
- [148] Osselin F, Soulaïne C, Fauguerolles C, Gaucher EC, Scaillet B, Pichavant M. Orange hydrogen is the new green. *Nat Geosci* 2022;15:765–9. <https://doi.org/10.1038/s41561-022-01043-9>
- [149] Pan B, Yin X, Iglauer S. Rock-fluid interfacial tension at subsurface conditions: implications for H₂, CO₂ and natural gas geo-storage. *Int J Hydrog Energy* 2021;46:25578–85. <https://doi.org/10.1016/j.ijhydene.2021.05.067>
- [150] Peng J, Xia B, Lu Y, Song R, Wang L. Pore-scale analysis and modeling of heterogeneous wettability in immiscible two-phase flow inside natural porous media. *Geoenergy Sci Eng* 2025;247:213676. <https://doi.org/10.1016/j.geoen.2025.213676>
- [151] Peng J, Xia B, Lu Y, Wang L, Song R. Pore-scale numerical investigation on the capillary trapping of hydrogen in natural sandstone under in-situ wettability condition: implications for underground hydrogen storage in aquifers. *Int J Hydrog Energy* 2025;113:509–22. <https://doi.org/10.1016/j.ijhydene.2025.02.480>
- [152] Perera MSA. A review of underground hydrogen storage in depleted gas reservoirs: insights into various rock-fluid interaction mechanisms and their impact on the process integrity. *Fuel* 2023;334:126677. <https://doi.org/10.1016/j.fuel.2022.126677>
- [153] Pini R, Benson SM. Simultaneous determination of capillary pressure and relative permeability curves from core-flooding experiments with various fluid pairs. *Water Resour Res* 2013;49:3516–30. <https://doi.org/10.1002/wrcr.20274>
- [154] Ponomar M, Krasnyuk E, Butylskii D, Nikonenko V, Wang Y, Jiang C, Xu T, Pismenskaya N. Sessile drop method: critical analysis and optimization for measuring the contact angle of an ion-exchange membrane surface. *Membranes* 2022;12:765. <https://doi.org/10.3390/membranes12080765>
- [155] Prigmore S, Okon-Akan OA, Egharevba IP, Ogbaga CC, Okoye PU, Epelle E, Okolie JA. Cushion gas consideration for underground hydrogen storage. *Encyclopedia* 2024;4:847–63. <https://doi.org/10.3390/encyclopedia4020054>
- [156] Pruno S, Coti C, Mantegazzi A, Pozzovivo V, Marzano F. Underground hydrogen gas storage: a comprehensive evaluation of reservoir rock integrity at reservoir conditions. In: 85th EAGE annual conference & exhibition; 2024. p. 1–5. <https://doi.org/10.3997/2214-4609.2024101104>
- [157] Raza A, Arif M, Glatz G, Mahmoud M, Al Kobaisi M, Alafnan S, Iglauer S. A holistic overview of underground hydrogen storage: influencing factors, current understanding, and outlook. *Fuel* 2022;330:125636. <https://doi.org/10.1016/J.FUEL.2022.125636>
- [158] Rezaei A, Hassanpouryouzband A, Molnar I, Derikvand Z, Haszeldine RS, Edlmann K. Relative permeability of hydrogen and aqueous brines in sandstones and carbonates at reservoir conditions. *Geophys Res Lett* 2022;49:e2022GL099433. <https://doi.org/10.1029/2022gl099433>
- [159] Roden EE. Geochemical and microbiological controls on dissimilatory iron reduction. *C. R. Geosci.* 2006;338:456–67. <https://doi.org/10.1016/j.crte.2006.04.009>
- [160] van Rooijen W, Hashemi L, Boon M, Farajzadeh R, Hajibeygi H. Microfluidics-based analysis of dynamic contact angles relevant for underground hydrogen storage. *Adv Water Resour* 2022;164:104221. <https://doi.org/10.1016/j.advwatres.2022.104221>
- [161] Rooney C, Tappero R, Nicholas S, Li Q. Wellbore cement alteration and roles of CO₂ and shale during underground hydrogen storage. *Appl Geochem* 2024;170:106088. URL: <https://doi.org/10.1016/j.apgeochem.2024.106088>. <https://libkey.io/10.1016/j.apgeochem.2024.106088>
- [162] Saeed M, Jadhawar P. Optimizing underground hydrogen storage in aquifers: the impact of cushion gas type. *Int J Hydrog Energy* 2024;52:1537–49. <https://doi.org/10.1016/j.ijhydene.2023.08.352>
- [163] Safari A, Esfandyari H, Sugai Y, Haghighi M, Zeinijahromi A, Sarmadivaleh M, Masoumi H. Computational fluid dynamics modeling of rock-liquid-H₂ contact angles: implications for underground hydrogen storage. *J Energy Storage* 2024;81:110475. <https://doi.org/10.1016/j.est.2024.110475>
- [164] Shahriar MF, Khanal A, Khan MI, Pandey R. Current status of underground hydrogen storage: perspective from storage loss, infrastructure, economic aspects, and hydrogen economy targets. *J Energy Storage* 2024;97:112773. <https://doi.org/10.1016/j.est.2024.112773>
- [165] Shi Z, Driba DL, Lopez Rivera N, Kariminasab M, Beckingham LE. A review of coupled geochemical-geomechanical impacts in subsurface CO₂, H₂, and air storage systems. *Energies* 2024;17:2928. <https://doi.org/10.3390/en17122928>
- [166] Shiran BS, Aarra M, An-Stepec BA, Heydolph B, Carlsen DL, Djurhuus K, Dopffel N. Effects of microbial activities on hydrogen storage efficiency in porous media. *Int J Hydrog Energy* 2025;154:150287. <https://doi.org/10.1016/j.ijhydene.2025.150287>
- [167] Silverii F, Maccaferri F, Richter G, Gonzalez Cansado B, Wang R, Hainzl S, Dahm T. Poroelectric model in a vertically sealed gas storage: a case study from cyclic injection/production in a carbonate aquifer. *Geophys J Int* 2021;227:1322–38. <https://doi.org/10.1093/gji/ggab268>
- [168] Singh K, Bultreys T, Raeini AQ, Shams M, Blunt MJ. New type of pore-snap-off and displacement correlations in imbibition. *J Colloid Interface Sci* 2022;609:384–92. <https://doi.org/10.1016/j.jcis.2021.11.109>
- [169] Song H, Lao J, Zhang L, Xie C, Wang Y. Underground hydrogen storage in reservoirs: pore-scale mechanisms and optimization of storage capacity and efficiency. *Appl Energy* 2023;337:120901. <https://doi.org/10.1016/j.apenergy.2023.120901>
- [170] Song R, Feng D, Hui G, Liu J, Yang C. Visualized experiments on the hydrogen transports and bubble ripening mechanism in porous reservoir of underground hydrogen storage. *Int J Hydrog Energy* 2025;105:326–44. <https://doi.org/10.1016/j.ijhydene.2025.01.194>
- [171] Spietz RL, Payne D, Kulkarni G, Metcalf WW, Roden EE, Boyd ES. Investigating abiotic and biotic mechanisms of pyrite reduction. *Front Microbiol* 2022;13:878387. <https://doi.org/10.3389/fmicb.2022.878387>
- [172] Spurin C, Bultreys T, Rücker M, Garfi G, Schlepütz CM, Novak V, Berg S, Blunt MJ, Krevor S. Real-time imaging reveals distinct pore-scale dynamics during transient and equilibrium subsurface multiphase flow. *Water Resour Res* 2020;56:e2020WR028287. <https://doi.org/10.1029/2020wr028287>
- [173] Spurin C, Callas C, Darraj N, Rücker M, Benson S. The importance and challenges associated with multi-scale heterogeneity for geological storage. *InterPore J.* 2025;2, IP260225–2. <https://doi.org/10.69631/ipj.v2i1nr76>
- [174] Spurin C, Ellman S, Bultreys T, Kurotori T, Benson S, Tchilepi HA. The role of injection method on residual trapping: insights into bridging scales and heterogeneity. *Adv Water Resour* 2025;197:104913. <https://doi.org/10.1016/j.advwatres.2025.104913>
- [175] Strobel G, Zawallich J, Hagemann B, Ganzer L, Ippisch O. Experimental and numerical investigation of microbial growth in two-phase saturated porous media at the pore-scale. *Sustain Energy Fuels* 2023;7:3939–48. <https://doi.org/10.1039/d3se00037k>
- [176] Tarkowski R, Uliasz-Misiak B. Towards underground hydrogen storage: a review of barriers. *Renew Sustain Energy Rev* 2022;162:112451. <https://doi.org/10.1016/j.rser.2022.112451>
- [177] Thaysen EM, Butler IB, Hassanpouryouzband A, Freitas D, Alvarez-Borges F, Krevor S, Heinemann N, Atwood R, Edlmann K. Pore-scale imaging of hydrogen displacement and trapping in porous media. *Int J Hydrog Energy* 2023;48:3091–106. <https://doi.org/10.1016/j.ijhydene.2022.10.153>
- [178] Thaysen EM, Butler IB, Hassanpouryouzband A, Spurin C, Freitas D, Rizzo R, Alvarez-Borges F, Atwood R, Edlmann K. Time-resolved 2D and 3D imaging of hydrogen and brine displacement processes in porous clastic sandstone. *J Colloid Interface Sci* 2025;694:137704. <https://doi.org/10.1016/j.jcis.2025.137704>
- [179] Thaysen EM, Jangda Z, Hassanpouryouzband A, Menke H, Singh K, Butler IB, Heinemann N, Edlmann K. Hydrogen wettability and capillary pressure in clastic sandstone for underground hydrogen storage. *J Energy Storage* 2024;97:112916. <https://doi.org/10.1016/j.est.2024.112916>

- [180] Thaysen EM, McMahon S, Strobel GJ, Butler IB, Ngwenya BT, Heinemann N, Wilkinson M, Hassanpouryouzband A, McDermott CI, Edlmann K. Estimating microbial growth and hydrogen consumption in hydrogen storage in porous media. *Renew Sustain Energy Rev* 2021;151:111481. <https://doi.org/10.1016/j.rser.2021.111481>
- [181] Thiagarajan SR, Emadi H, Hussain A, Fernandez DM, Ispas I, Henderson SK, Watson M. Long-term effects of hydrogen and brine on the geomechanical properties of Berea sandstone—an experimental study. *Gas Sci Eng* 2025;139:205628. <https://doi.org/10.1016/j.jgsce.2025.205628>
- [182] Thiagarajan SR, Emadi H, Hussain A, Patange P, Watson M. A comprehensive review of the mechanisms and efficiency of underground hydrogen storage. *J Energy Storage* 2022;51:104490. <https://doi.org/10.1016/j.est.2022.104490>
- [183] Truche L, Berger G, Destigneville C, Guillaume D, Giffaut E. Kinetics of pyrite to pyrrhotite reduction by hydrogen in calcite buffered solutions between 90 and 180 °C: implications for nuclear waste disposal. *Geochim Cosmochim Acta* 2010;74:2894–914. <https://doi.org/10.1016/j.gca.2010.02.027>
- [184] Ugarte ER, Salehi S. A review on well integrity issues for underground hydrogen storage. *J Energy Resour Technol* 2022;144:1–27. <https://doi.org/10.1115/1.4052626>
- [185] Valverde-Isorna L, Ali D, Hogg D, Abdel-Wahab M. Modelling the performance of wind-hydrogen energy systems: case study the hydrogen office in Scotland/UK. *Renew Sustain Energy Rev* 2016;53:1313–32. <https://doi.org/10.1016/j.rser.2015.08.044>
- [186] Vasile NS. A comprehensive review of biogeochemical modeling of underground hydrogen storage: a step forward in achieving a multi-scale approach. *Energies* 2024;17:6094. <https://doi.org/10.3390/en17236094>
- [187] Vasile NS, Bellini R, Bassani I, Vizzarro A, Abdel Azim A, Coti C, Barbieri D, Scapolo M, Viberti D, Verga F, Pirri F, Menin B. Innovative high pressure/high temperature, multi-sensing bioreactors system for microbial risk assessment in underground hydrogen storage. *Int J Hydrog Energy* 2024;51:41–50. <https://doi.org/10.1016/j.ijhydene.2023.10.245>
- [188] Veshareh MJ, Thaysen EM, Nick HM. Feasibility of hydrogen storage in depleted hydrocarbon chalk reservoirs: assessment of biochemical and chemical effects. *Appl Energy* 2022;323:119575. <https://doi.org/10.1016/j.apenergy.2022.119575>
- [189] Vítězová M, Onderka V, Urbanová I, Molíková A, Hanišáková N, Buriánková I, Vítěz T, Novák D, Lochman J, Macháľková M, Javůrek J. In situ field experiment shows the potential of methanogenic archaea for biomethane production from underground gas storage in natural rock environment. *Environ Technol Innov* 2023;32:103253. <https://doi.org/10.1016/j.eti.2023.103253>
- [190] Wallace RL, Cai Z, Zhang H, Zhang K, Guo C. Utility-scale subsurface hydrogen storage: UK perspectives and technology. *Int J Hydrog Energy* 2021;46:25137–59. <https://doi.org/10.1016/j.ijhydene.2021.05.034>
- [191] Wang G, Beteta A, Sorbie KS, Mackay EJ. Inherent errors in current core-flooding relative permeability data for modelling underground hydrogen storage. *InterPore J*. 2025;2, IPJ260225–6. <https://doi.org/10.69631/ipj.v2i1nr42>
- [192] Wang J, Yang Y, Cai S, Yao J, Xie Q. Pore-scale modelling on hydrogen transport in porous media: implications for hydrogen storage in saline aquifers. *Int J Hydrog Energy* 2023;48:13922–33. <https://doi.org/10.1016/j.ijhydene.2022.11.299>
- [193] Wang S, Mu Y, Gao Y, Yuan M, Pan S, Tang Y, Wang K. Influence of injection and withdrawal rates on hydrogen distribution in sandstone: implications for hydrogen storage in porous reservoirs. *Int J Hydrog Energy* 2024;90:1263–70. <https://doi.org/10.1016/j.ijhydene.2024.10.065>
- [194] Wang S, Pan S, Tang Y, Gao Y, Wang K. Experimental study of hydrogen flow behavior in sandstone at the core scale during cyclic hydrogen and water injections. *J Energy Storage* 2025;123:116810. <https://doi.org/10.1016/j.est.2025.116810>
- [195] Wang Y, Chakrapani TH, Wen Z, Hajibeygi H. Pore-scale simulation of H₂-brine system relevant for underground hydrogen storage: a lattice Boltzmann investigation. *Adv Water Resour* 2024;190:104756. <https://doi.org/10.1016/j.advwatres.2024.104756>
- [196] Xiong Z, Hou J, Du Q, Chen Z, Lu X, Liu Y, Wei B, Lu T. A comprehensive review of H₂ physical behavior and H₂-rock-microbial interactions in underground hydrogen storage. *Energy (Oxf)* 2025;326:136226. <https://doi.org/10.1016/j.energy.2025.136226>
- [197] Yang S, Suo S, Gan Y, Bagheri S, Wang L, Revstedt J. Experimental study on hysteresis during cyclic injection in hierarchical porous media. *Water Resour Res* 2025;61:e2024WR038923. <https://doi.org/10.1029/2024wr038923>
- [198] Yekta AE, Manceau JC, Gaboreau S, Pichavant M, Audigane P. Determination of hydrogen–water relative permeability and capillary pressure in sandstone: application to underground hydrogen injection in sedimentary formations. *Transp Porous Media* 2018;122:333–56. <https://doi.org/10.1007/s11242-018-1004-7>
- [199] Yekta AE, Pichavant M, Audigane P. Evaluation of geochemical reactivity of hydrogen in sandstone: application to geological storage. *Appl Geochem* 2018;95:182–94. <https://doi.org/10.1016/j.apgeochem.2018.05.021>
- [200] Zeng L, Sander R, Chen Y, Xie Q. Hydrogen storage performance during underground hydrogen storage in depleted gas reservoirs: a review. *Engineering (Beijing)* 2024. <https://doi.org/10.1016/j.eng.2024.03.011>
- [201] Zeng L, Vialle S, Ennis-King J, Esteban L, Sarmadivaleh M, Sarout J, Dautriat J, Giwelli A, Xie Q. Role of geochemical reactions on caprock integrity during underground hydrogen storage. *SSRN Electron J* 2022;65:107414. <https://doi.org/10.2139/ssrn.4233860>
- [202] Zhan S, Zeng L, Al-Yaseri A, Sarmadivaleh M, Xie Q. Geochemical modelling on the role of redox reactions during hydrogen underground storage in porous media. *Int J Hydrog Energy* 2024;50:19–35. <https://doi.org/10.1016/j.ijhydene.2023.06.153>
- [203] Zhang G, Regaieg M, Blunt MJ, Bijeljic B. Primary drainage and waterflood capillary pressures and fluid displacement in a mixed-wet microporous reservoir carbonate. *J Hydrol* 2023;625:130022. <https://doi.org/10.1016/j.jhydrol.2023.130022>
- [204] Zhang H, Zhang Y, Al Kobaisi M, Iglauer S, Arif M. Effect of cyclic hysteretic multiphase flow on underground hydrogen storage: a numerical investigation. *Int J Hydrog Energy* 2024;49:336–50. URL: <https://doi.org/10.1016/j.ijhydene.2023.08.169>. <https://www.sciencedirect.com/science/article/pii/S036031992304171X>
- [205] Zhang Q, Geiger S, Storms JE, Voskov DV, Jackson MD, Hampson GJ, Jacquemyn C, Martinius AW. Capillary pinning in sedimentary rocks for CO₂ storage: mechanisms, terminology and state-of-the-art. *Int J Greenh Gas Control* 2025;144:104385. <https://doi.org/10.1016/j.ijggc.2025.104385>
- [206] Zhang Y, Bijeljic B, Gao Y, Goodarzi S, Foroughi S, Blunt MJ. Pore-scale observations of hydrogen trapping and migration in porous rock: demonstrating the effect of ostwald ripening. *Geophys Res Lett* 2023;50:e2022GL102383. <https://doi.org/10.1029/2022gl102383>
- [207] Zhao Q, Wang Y, Chen C. Numerical simulation of the impact of different cushion gases on underground hydrogen storage in aquifers based on an experimentally-benchmarked equation-of-state. *Int J Hydrog Energy* 2024;50:495–511. <https://doi.org/10.1016/j.ijhydene.2023.07.262>
- [208] Zhou JD, Kovscek A. Viscous-dominated flow experiments for hydrogen storage in saline aquifers. In: *SPE Western regional meeting*; 2025. <https://doi.org/10.2118/224189-ms>, p. D021S011R002.
- [209] Zivar D, Kumar S, Foroozesh J. Underground hydrogen storage: a comprehensive review. *Int J Hydrog Energy* 2021;46:23436–62. <https://doi.org/10.1016/j.ijhydene.2020.08.138>