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Invited review

Phase equilibrium, thermodynamics, hydrogen-induced effects and the interplay mechanisms in underground hydrogen storage

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Abstract:
Global attention has shifted back to hydrogen, the ultimate green alternative energy, due to the intensifying extreme climate and greenhouse impacts. It is now a promising energy carrier for large-scale underground hydrogen storage, which may benefit the peak-shaving of electric grids and the supply from other sustainable energies. The prospects of underground hydrogen storage are bright due to the abundance of subsurface formations such as depleted oil and gas reservoirs, saline aquifers, and salt caverns and the traditional energy industry's extensive underground procedures and management knowledge. However, hydrogen's unique thermodynamic and chemical properties pose challenges as well, requiring further research and modeling to provide a firm basis and validate engineering practice. Some typical concerns, like hydrogen embrittlement, have long plagued industry. The intricate and difficult-to-reach nature of the underground makes fundamental mechanics, mathematical modeling, and numerical simulation essential tools for further advancement. Integration of experiments and simulations at the multi-scale (molecular, pore, and Darcy) provides data support and solution validation for the pursuit of comprehensive descriptions and accurate predictions of hydrogen storage and extraction processes. Given this, our paper reviews the thermodynamic properties of hydrogen, focuses on the phase equilibrium processes at different scales in underground hydrogen storage, and introduces the related mathematical models and simulation methods. Based on recent research progress and comparing four typical trapping mechanisms in carbon capture, utilization and storage, we highlight some unique hydrogen-induced effects: (1) compositional grading; (2) competitive adsorption; (3) hydrogen-induced rock alteration, in conjunction with phase equilibrium issues, discuss their interplay mechanisms, offering constructive insights for further in-depth research.

1. Introduction

As the most abundant element in the universe, hydrogen is ubiquitous in daily life. People's naive affection for it stems not only from its role as a component of water, the source of life, but also from our discoveries over the centuries. Since the 18th century, the journey began with the production of hydrogen through the electrolysis of water, progressing to its recognition as the ultimate green energy source. Further exploration on its properties led to the discovery of nuclear fusion reactions and the immense energy released, prompting some idealistic scientific concepts such as the "artificial sun". The relationship between the hydrogen element and energy has been intricately intertwined over the years.

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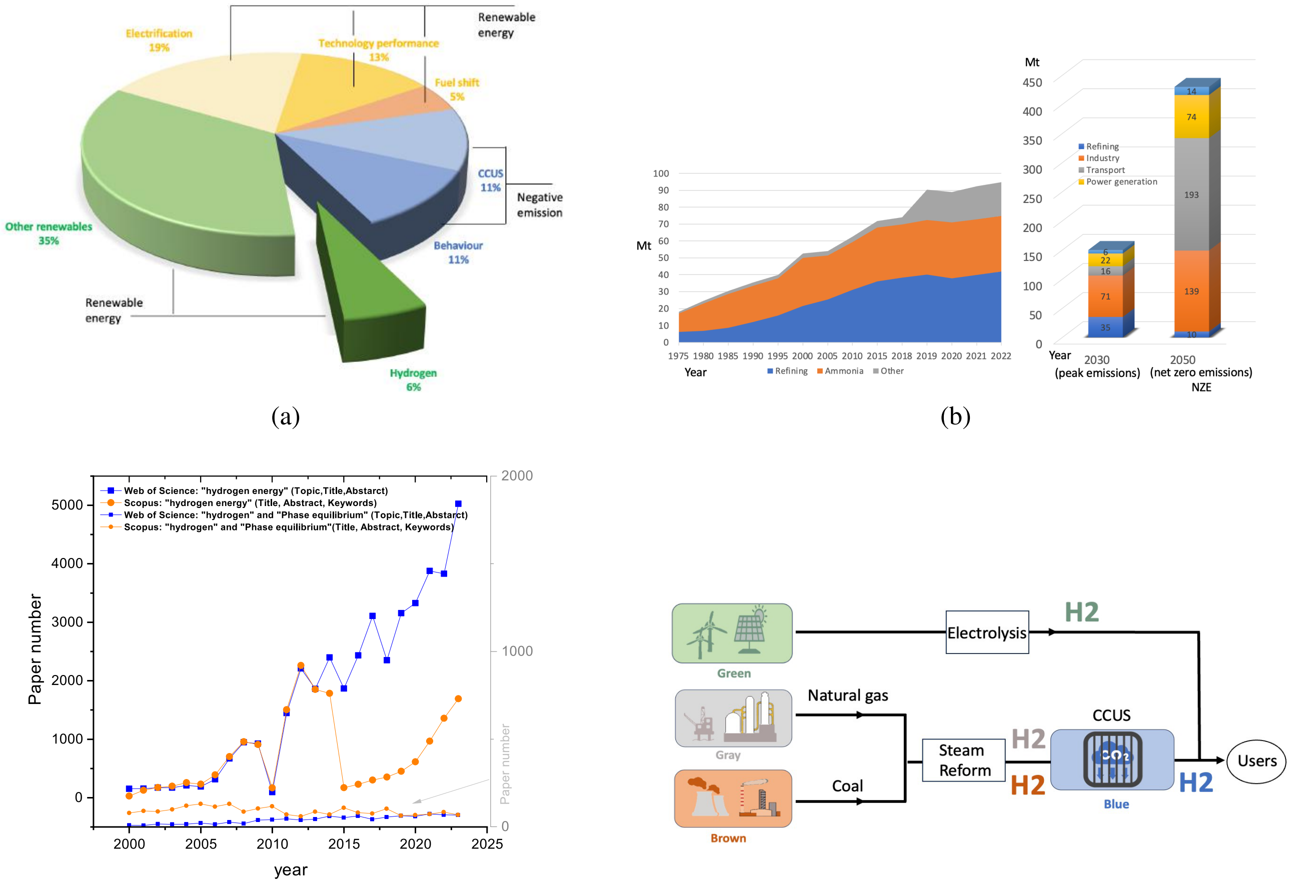


(a) (b)

(c) (d)

Fig. 1. Some statistics and schematics about hydrogen energy: (a) the pie plot of the cumulative emissions reduction for NZE by 2050, source: IEA; (b) the global hydrogen demand in recent decades and the projection for 2030 and 2050, source: IEA; (c) statistics on published research papers related to hydrogen energy, source: Scopus & Web of Science; (d) the schematic for the classification of hydrogen.

As shown in Figs. 1(b) and 1(d), the global consumption of hydrogen is mainly reflected in its role as an industrial ingredient: production of ammonia and its refining function. Hydrogen is used as a feedstock in the Haber-Bosch process: $N_2+3H_2 \rightleftharpoons 2NH_3$ to synthesize ammonia, which is a critical component of many fertilizers. It is also utilized to remove sulfur from fuels and to process heavy crude oils into lighter, more useful products. The primary method of hydrogen production still relies on the classical steam methane reforming (SMR): $CH_4+H_2O \rightleftharpoons CO+3H_2$. From the perspective of hydrogen's entire lifecycle and the goal of carbon neutrality, not only does hydrogen storage involve underground technologies, but the carbon capture, utilization and storage (CCUS) (Bao et al., 2016), which shifts "grey hydrogen" and "brown hydrogen" to "blue hydrogen", to achieve the mission on decarbonization. Integrating CCUS and underground hydrogen storage (UHS) aids energy transition and promotes hydrogen industry as well. The follow-up of the article will also compare and analyze the two of them.

As a fuel, the remarkable success of hydrogen as rocket fuel in space missions has solidified its status as the highest mass-energy density (Zhang et al., 2021). After returning to Earth, there is still a long way to go before it becomes a major contributor to the world energy matrix. But any tiny step in hydrogen technology can lead to transformative changes in energy-intensive industries (Neuwirth et al., 2022). Although relentless pursuit and substantial efforts have been put into finding green catalytic hydrogen production and material development, including metal hydrides (Wang et al., 2011), carbon nanotubes, hydrogen hydrates (Song et al., 2021), polymer coatings (Michler and Naumann, 2009), carbon fiber, and thermal insulation solutions for compressed and liquefied tanks for their portability and efficiency (Schlapbach and Züttel, 2001; Andreas, 2004), we are still stuck in the economical dilemma.

Fortunately, the urgent demand for alternative, clean energy arises from the escalating frequency of extreme weather and global warming. In alignment with the objectives of the Paris Agreement, nations worldwide are devising strategies to mitigate these challenges. Prominent initiatives include China's commitment to achieving a carbon peak in 2030 and net-zero emissions (NZE) in 2050, the EU's European Green

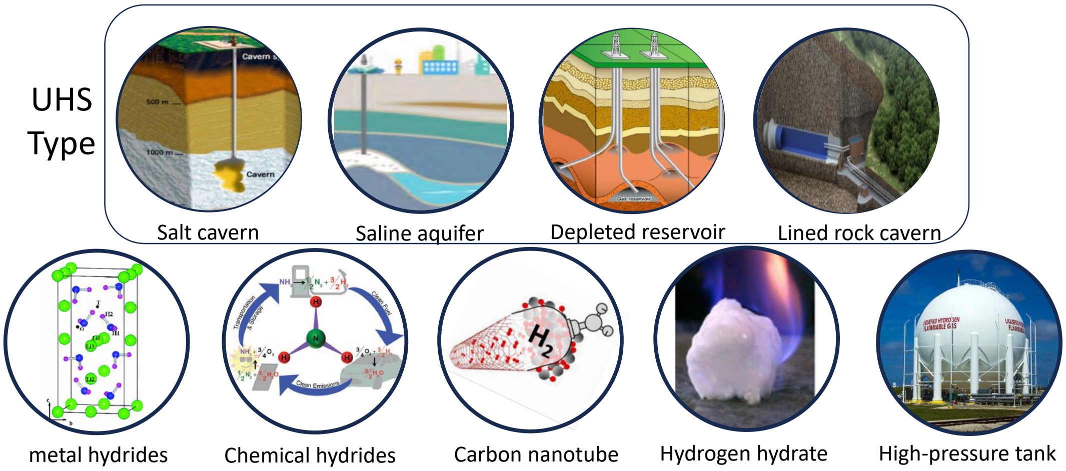


Fig. 2. The types of hydrogen storage.

Deal, and the return of the US to that deal. To achieve this goal, hydrogen energy is expected to contribute to 6% of the cumulative emissions reduction. Additionally, the total demand for hydrogen needs to increase to four times its current level as shown in Figs. 1(a) and 1(b). Environmental pressure will inevitably bring more powerful policy support. Unlike before, hydrogen is now coming into focus again as a promising energy carrier in large-scale underground energy storage. The types of hydrogen energy storage are shown in Fig. 2.

It is worth mentioning that a lot of progress on electrification in the automotive industry has been achieved via not only US pioneering companies like Tesla but also China's rapid catch-up and overtaking in related industries. Now, China has dominated the global electric vehicle market and has an overwhelming scale of electrical infrastructure. Also, China's renewable power generation leads the world by a significant margin. Natural factors such as weather, day-night shifts, seasons, and geographical conditions influence these solar, wind, tide, and geothermal energy productions. However, the continuous fluctuations between renewable input and user demand can lead to surpluses and deficits. With the increasing share of renewable energy and electrical transportation, particularly given China's large population and active economic activities, the increase in grid loading and the severity of variability are inevitable. The UHS is considered a promising solution to take advantage of this variability as shown in Fig. 3. A certain number of UHS operational cases have been identified (Liu et al., 2023; Song et al., 2023). The technological accumulation and extensive management experience of the traditional energy industry have laid a solid foundation for the UHS. All these indicate a promising outlook for hydrogen energy storage.

But then again, it is impractical to directly convert current storage sites into UHS. After all, due to its unique thermodynamic and chemical properties, hydrogen can introduce a series of new challenges, such as the notorious problem of hydrogen embrittlement (Li et al., 2020). Along with the accessibility issues of underground environments, phenomena and mechanisms that span from nanostructures to vast geological formations result in complex processes marked by multi-phase, multi-component, and multi-scale interactions. Fundamental studies, mathematical modeling, and numerical simulations are crucial for conducting feasibility investigations like site selection and making informed management decisions. There are countless comprehensive review work about the UHS (Bai et al., 2014; Tarkowski, 2019; Heinemann et al., 2021; Zivar et al., 2021; Miocic et al., 2023). This paper focuses on phase equilibrium and thermodynamic process aspects in UHS, which did not receive sufficient research attention as shown in Fig. 1(c). We specifically review the mathematical modeling approaches across different scales for the UHS. Compared with the classic four kinds of trapping mechanisms in carbon sequestration projects (Zhang and Song, 2014; Khandoozi et al., 2023) and based on the uniqueness of hydrogen, we highlight three hydrogen-induced mechanisms: (1) compositional grading; (2) competitive adsorption; (3) hydrogen-induced rock alteration. Additionally, we explore how phase equilibrium processes and thermodynamic properties at various scales affect these trapping mechanisms, ultimately impacting the safety and efficiency of UHS.

The rest of this paper is organized as follows: In section 2, some typical thermodynamic properties of hydrogen are reviewed. In section 3, we sort out common density models, such as equations of states (EoSs) and viscosity models, to describe real gas and its mixture fluids in the UHS. Next, phase equilibrium calculation frameworks that span different scales—reservoir scale and pore scale—are introduced in conjunction with some molecular scale works on the UHS. In section 4, compared with traditional reservoir and CO_2 sequestration, we analyze these four basic trapping mechanisms in UHS and CCUS to demonstrate their differences, highlight three unique hydrogen-induced effects, and present how they interplay with the phase equilibrium processes. In section 5, a conclusion and some constructive advice and remarks on the UHS are given.

2. Thermodynamics of hydrogen

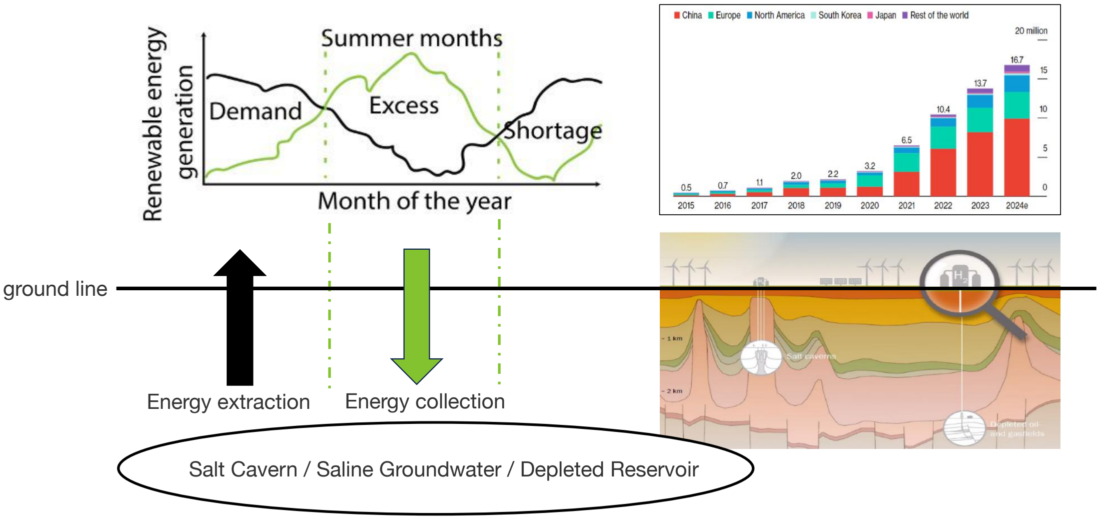


Fig. 3. The schematic of underground hydrogen storage adapted from (Talukdar et al., 2024) and the statistic on global electric vehicle market share, source: TNO & BloombergNEF.

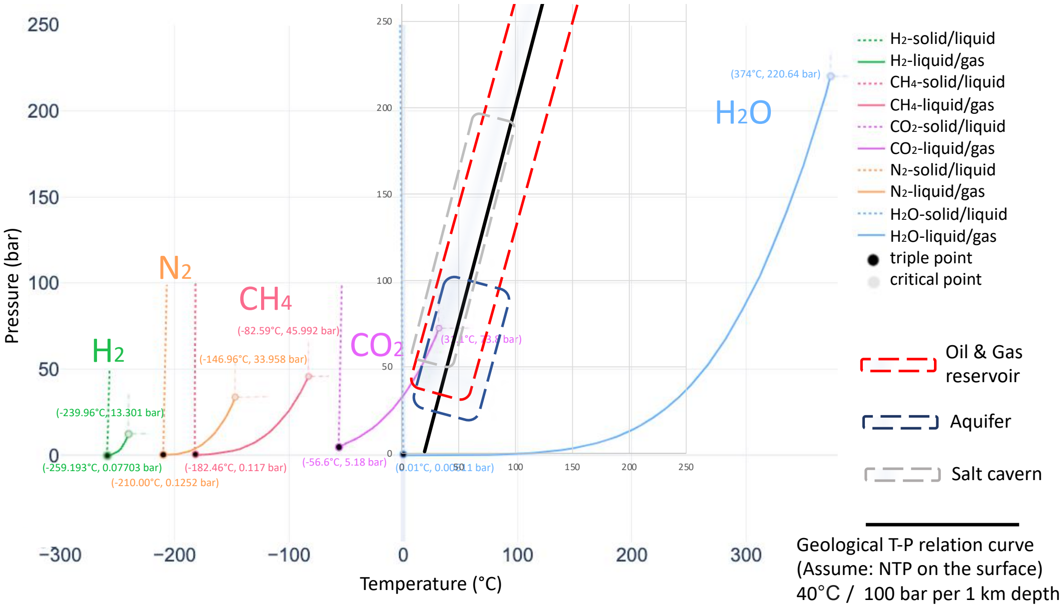


Fig. 4. Phase diagrams for hydrogen and some other common gases in the UHS and T-P ranges of different underground storage sites.

2.1 Density

Given its minimal molecular mass, hydrogen gas exhibits the lowest density among substances under identical thermodynamic conditions. Compared to common underground gases like methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), and water vapor (H_2O), the density of H_2 is significantly lower, often by an order of magnitude. This disparity is even more pronounced when comparing hydrogen to fluids such as oil and saline water, leading to distinct flow and displacement patterns in UHS. The very low critical temperature and extremely narrow liquid-phase region of hydrogen make it hard to liquefy even at high pressure. In certain geological storage sites, fluids may include critical CO_2 as shown in Fig. 4, presenting significant density contrast challenges. The contrast will cause and exacerbate phenomena such as gravity override and gravity tongue (Berg and Ott, 2012), both of which are manifestations of gravity segregation (Feldmann et al., 2016; Mahdi et al., 2021; Nazari et al., 2024;). Moreover, the gravity segregation is influenced by the position of the well bottom in UHS. As the injection depth increases, the impacts of gravity segregation become more pronounced, favoring upward migration of H_2 and potentially affecting storage performance and reproduction efficiency. It also indicates the significance of compositional grading in UHS (Li et al., 2017; Sun, 2019; Zhou et al., 2024), a concept that covers a wider range of mechanisms for creating gradient distributions, including temperature, capillarity, and more. To mitigate these issues, a cushion gas between hydrogen and the saline or depleted hydrocarbon fluid is recommended. Unlike porous media storage formations, salt caverns with large cavities may experience more severe flow instability due to fierce convection.

2.2 Viscosity

The low viscosity of hydrogen can create a significant difference in fluidity compared to other fluids, inducing phenomena like viscous fingering (Feldmann et al., 2016; Hogeweg et al., 2024; Zhang et al., 2024; Zhu et al., 2024). As it displaces saline water or oil, this viscosity contrast steers hydrogen into specific channels within heterogeneous layers, leading to uncontrollable lateral spread and finger-like flow patterns. Such a spread complicates the future recovery. The broad lateral extent of plumes and complex flows during imbibition phases may lead to more hydrogen gas pockets and unrecoverable areas. Even though there is interplay with capillary trapping and wettability, of course, the H_2 capillary pressure hysteresis can also be intensified by this viscosity difference. Minimizing viscous fingering and gravity override is a vital factor to diminish working gas stranding and improve recovery efficiency. Thus, optimized injection rates and cushion gas selection are important for UHS.

2.3 Diffusion

The small molecule size and lightest mass of H_2 result in a remarkably large diffusion coefficient in both the gas and liquid phases. This rapid diffusion increases contact with reservoir substances, promoting chemical reactions with microorganisms or mineral ions in underground environments. This significant diffusion ability can also lead to undesired mixing with cushion gases, compromising hydrogen purity. Furthermore, it enhances the leakage risks, even for the tight caprock. Moreover, its colorless, odorless nature makes leaks difficult to detect and Its broad ignition range makes very stringent safety measures necessary. Additionally, the diffusivity makes it prone to transport in micro-structures of metal and cause hydrogen embrittlement, requiring high-quality and corrosion-resistant materials and extra coating for subsurface equipment, including casing pipes, valves, pumps, even cement and rubber (Taleghani and Santos, 2023; Fernandez et al., 2024). The quality of well completion deserves close attention because of its influence on the UHS's sealing performance.

2.4 Solubility

The solubility of H_2, compared to CO_2 in saline, is very weak; thus, many numerical simulations either neglect it or simplify its representation through a basic Henry's law constant. Although the quantity of solubility trapping contributing to total H_2 storage is minor, a precise prediction of the composition partition in the system is still important since the moisture and the ion concentration in solution determine the pH value of the system and the geochemical reaction tendency and rate. For example, the moisture content is critical for biochemical reactions involving sulfate reduction. Even minor perturbations in hydrogen concentration can disrupt and reset the entire thermodynamic and phase equilibrium, not to mention the significant fluctuations in H_2 quantities during injection and extraction. The research on these mechanisms and their interplay must rely on accurate phase equilibrium and thermodynamic property prediction. The solubility of H_2 in water slightly increases with temperature and significantly with pressure, but decreases sharply with the increasing molality of the formation brine (Buscheck et al., 2024). These dynamics and tendencies cannot be ignored, and the phase equilibrium prediction module acts as an essential part of robust and reliable compositional simulators (Cai et al., 2022; Chai et al., 2023; Huang et al., 2023).

2.5 Interfacial tension and wettability

The interfacial tension (IFT) between hydrogen and brine, as well as between cushion gas and brine, plays a crucial role in determining flow patterns, capillary (residual) trapping, and displacement performance. It varies with pressure, temperature, and brine salinity, which are strongly related to the thermodynamic state. Extending a two-phase system to three-phase interactions introduces wettability and contact angle problems, which are essential for understanding drainage and imbibition processes. The formation of gas pockets and the gas aggregation process impact hydrogen recovery, either negatively or positively. Studies on how IFT and wetabbility change with hydrogen content, pH value, salinity, rock type, and other various thermodynamic conditions can offer insights for injection and recovery strategies. Additionally, the assessment of H_2 wettability on various rock materials aids in the selection of suitable geological storage sites. A critical component of ensuring the integrity of the UHS is the water in the wet caprock layer, which, thanks to its capillary effect, prevents hydrogen escape and enhances the storage integrity of the enclosure, minimizing hydrogen losses. We also refer to this mechanism as capillary sealing.

2.6 Activity

Hydrogen, rarely found in pure substance form on Earth, is highly reactive due to its electron configuration, which resembles that of active metals. This predisposes hydrogen atoms to form compounds by either sharing or transferring an electron with other atoms, leading to a lower energy state (Wang et al., 2024). Despite showing stability like an inertia gas in subsurface conditions where it does not react directly with other common gases, hydrogen can fuel the metabolism of archaea and bacteria, a seemingly advantageous trait for UHS. Microorganism-catalyzed conditions underground activate the hydrogen's reactivity. Sulfate and carbonate, in particular, can react with hydrogen in processes such as methanogenesis and sulfate reduction, resulting in hydrogen loss. These reactions can produce corrosive by-products like H_2S, potentially compromising the purity of stored hydrogen, degrading metal surfaces, and providing a preferred path for hydrogen embrittlement. In some operating underground storage projects involving hydrogen gas mixtures, a significant increase in CH_4 concentration was noted within just seven months, while H_2 and CO_2 concentrations diminished (Amigáň et al., 1990; Liu et al., 2023).

Previous UHS research has repeatedly reviewed or individually studied these special hydrogen properties. Here, we empathize with the interplay between phase quilibrium and them. The upcoming content will introduce some new thoughts and suggestions on phase equilibrium calculation in UHS.

3. Phase equilibrium crossing scales in UHS

Before delving into this section, we reiterate the importance of accurately predicting and describing the partitioning of compositions—not only hydrogen and cushion gas but also water vapor, ions in brine, microbial elements, and potential abandoned hydrocarbons in depleted hydrocarbon reservoirs. The precision of the phase equilibrium calculation is crucial as it significantly influences the quantitative descriptions of chemical reactions, the measurement of hydrogen purity and loss, and the assessment of the integrity of reservoir traps, ultimately impacting safety and economic indicators. Besides, the development of a comprehensive and precise UHS simulator must incorporate this necessary module with more advanced mathematical models and computational algorithms. As a result, recent studies and advancements in UHS phase equilibrium merit attention.

3.1 Static phase equilibrium at Darcy scale

The traditional oil and gas industry employs cubic equations of state (EoS), often for phase equilibrium calculation (also called flash calculation), especially the widely recognized Peng-Robinson equation (PR) (Feng et al., 2022). The development of cubic EoSs originated from the characterization of real gas behavior, leading to models modified from the ideal gas law by accounting for the volume of gas molecules and their interactions. Another developmental path is purely empirical, relying on fitting data to the Virial EoS form, exemplified by the Benedict-Webb-Rubin EoS (BWRS) (Zhang et al., 2021). With the ongoing accumulation of industrial experience and on-site data, comprehensive models like GERG 2004, GERG 2008, AGA, and others have been developed to meet industrial requirements, and many UHS simulators and research studies adopt these EoSs for their research (Zhao et al., 2024). The perturbed chain statistical associating fluid theory (PC-SAFT) EoS (Kou and Li, 2019), grounded in perturbation theory and statistical thermodynamics, stands out because of its theory-based advancement among EoSs for studying complex scientific mechanisms. This approach enhances the model by incorporating associative terms into the residual free energy expression, accommodating a wider variety of intermolecular interactions, including those involving ions and hydrogen bonding. A notable hybrid method, the Cubic-Plus-Association (CPA) method, combines cubic EoSs with associative terms to improve its applicability. The current classic frameworks for phase equilibrium calculations are primarily based on NPT (constant number of particles, pressure, and temperature) and NVT (constant number of particles, volume, and temperature) ensembles, which correspond to the minimization of Gibbs free energy and Helmholtz free energy, respectively. We can divide computational approaches into two main categories: those that solve the non-linear equation system for chemical potential equilibrium and those that directly optimize the free energy function. While viscosity is typically considered a transport property, its modeling often employs dimensionless analysis, the similarity principle, or the Chapman-Enskog theory. The similarity principle encompasses EoSs-based viscosity models, such as the PRμ model. Recent advancements in scaling methods make use of the thermodynamic property of excess entropy. The above typical classifications of EoSs and viscosity models are illustrated in Fig. 5.

For the **NVT** system, equilibrium is achieved by minimizing the Helmholtz free energy F, considering both gas (G) and liquid (L) phases, where the total volume V and total compositions $\mathbf{N}$ are fixed. Based on the thermodynamic relations ($\mu_i = \partial F / \partial N_i$ and $-p = \partial F / \partial V$), we can derive balance relations for the chemical potential μ_i of each component and phase pressure p as:

$$\mu_i^G - \mu_i^L = 0$$
$$p^G - p^L = 0$$

For the **NPT** system, Gibbs free energy G minimization also dictates equilibrium, leading to the chemical potential balance:

$$\mu_i^G = \mu_i^L$$

Defining fugacity f as "effective partial pressure", chemical potential will be ($\mu = \mu^0 + RT\ln\left(f / P^0\right)$). Then this balance relationship can be converted into:

$$f_i^V = f_i^L$$

Introducing fugacity coefficient $\phi_i = f_i / p$ and equilibrium ratio $K_i = \phi_i^L / \phi_i^G$, along with phase fraction $\beta = N^G / N^L$, the non-linear system of balance relations can be reformulated with mass conservation as follows:

$$K_i = K_i\left(T, p, x_1\left(\beta, K_1\right), \cdots, y_M\left(\beta, K_M\right)\right)$$
$$\sum_{i=1}^{M} \frac{\left(K_i - 1\right) z_i}{1 + \beta\left(K_i - 1\right)} = 0$$

Solving this system for K_i and β typically employs the Newton methods or the successive substitution iteration method (SSI), requiring a good initial guess (via Wilson's correlation or phase stability testing) (Li et al., 2018; Feng et al., 2022). Alternatively, optimization methods like the convex hull or branch and bound can minimize the free energy function (Jindrová and Mikyška, 2013) and determine the unknowns. Regardless of the methods, adherence to thermodynamic consistency ensures the process minimizes energy, namely aligning with the principle of entropy increase ($dF = dU - TdS$). Over the last few decades, numerous thermodynamic models and phase equilibrium prediction methods have been developed to address CH_4 or other gases like CO_2 in pure water or brine, including fugacity coefficient models (various EoSs) and activity coefficient models.

However, there is a limited amount of literature on the phase equilibrium of hydrogen mixtures with brine or water systems, particularly in geological reservoirs. Leveraging the

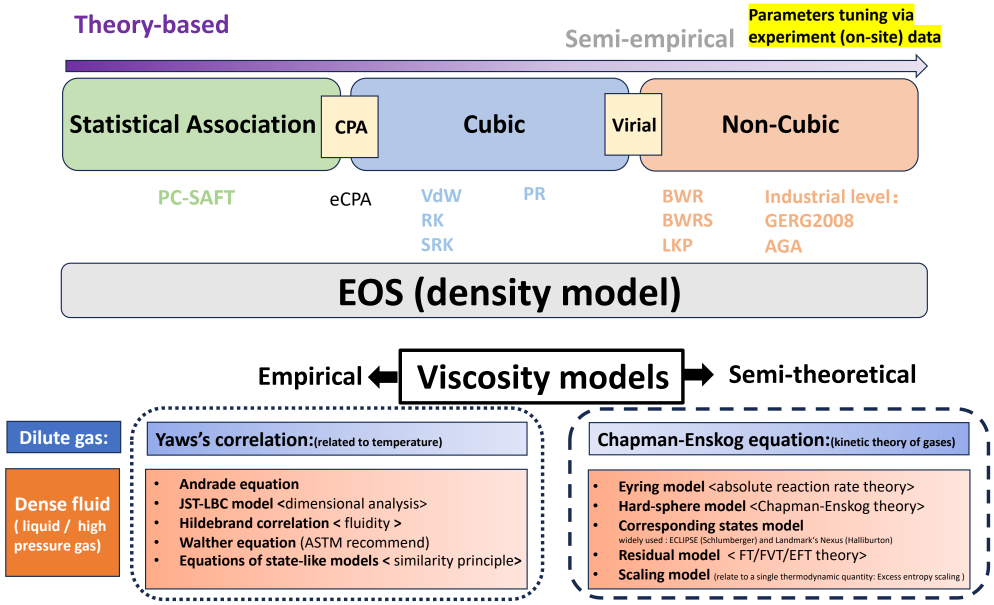


Fig. 5. The classification of equations of states (EoSs) and viscosity models.

discussed phase equilibrium calculation framework, we review some valuable literature contributions to this circle and industry. A traditional cubic PR EoS, along with a dynamic model based on the NVT flash framework, was employed to study the phase equilibrium of common gas mixtures (CH_4, CO_2, H_2) in the hydrogen industry, especially in SMR processes, presenting significant phase equilibrium data, including phase stability testing and the tangent plane distance function as shown in Fig. 6(d) (Zhang et al., 2022). The reliability of various cubic EoSs (such as PR, SRK), their modifications (SR-RK), and non-cubic EoSs (PC-SAFT and GERG2008) was benchmarked for predicting phase equilibrium and thermophysical properties of binary and ternary H_2-blend mixtures (including CH_4, C_2H_6, C_3H_8, H_2S, CO_2, CO, H_2O and N_2) common in H_2 geo-storage processes. The SR-RK EoS was found to be the most effective among cubic EoSs, while non-cubic EoSs, PC-SAFT and GERG2008, showed superior accuracy in density predictions and were recommended for use in compositional simulators (Zhao et al., 2024). Their sensitivity analysis indicated significant vapor-liquid equilibrium (VLE) envelope changes with varying H_2 concentrations (Alanazi et al., 2022). A model for predicting hydrogen solubility in the H_2-H_2O-NaCl system using a polynomial expression demonstrated good accuracy within UHS condition ranges, extendable to more complex solutions by incorporating the fugacity of the gas mixture and the activity of the mixed electrolyte solution (Li et al., 2018).

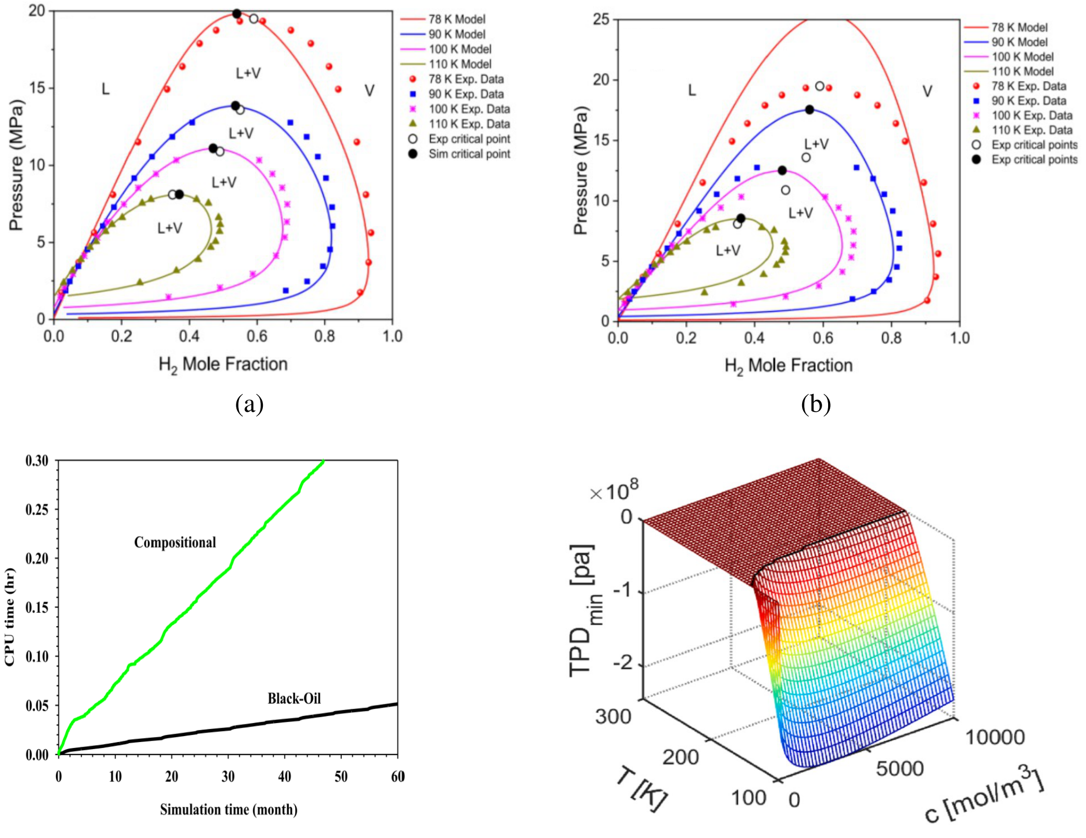
Even though the solubility of H_2 is not comparable with CO_2, no matter for both UHS and CCUS projects, the same difficulty comes from the treatment of the electrolyte. Many solubility calculations and phase equilibrium calculations have successfully predicted the CO_2-saline system, and some valuable research experiences from these CO_2 examples can be gained for hydrogen. It is observed that general cubic EoSs may lose accuracy when modeling the equilibrium of the H_2-brine-other gases system, and some advanced EoSs that account for ions, hydrogen bonding, and other complex interactions generally perform better. The cubic EoS SR-RK model is still good at predicting the VLE envelope in some cases, though, as shown in Figs. 6(a) and 6(b). Thus, when dealing with the phase equilibrium of the H_2-H_{20}-NaCl system, a reasonable choice goes to the CPA approach. It might be a better choice than using PC-SAFT directly because, on the one hand, it enjoys good capability like SR-RK in VLE envelope prediction; on the other hand, it strikes a good balance between computational efficiency and accuracy (Li et al., 2020). Here are some state-of-the-art approaches for modeling ionic liquid systems:

1) Irregular ionic lattice models (considering ionic liquids a liquid salt composed of ions to use lattice theory);
2) Regular solution theory (using activity coefficient methods: UNIQUAC, NRTL);
3) Advanced Cubic EoSs or mixing rules;
4) The PC-SAFT or CPA model (more adjustable parameters & computational complexity);
5) The group contribution methods.

It is important to note that two primary methods exist for performing phase equilibrium calculations. Method (1) employs EoSs for both gas and liquid phases to derive balance equations. However, this approach might struggle with complex solutions and high-pressure conditions due to its reliance on gas laws. Method (2) combines fugacity coefficient models for the gas phase with activity coefficient models for the liquid phase or solutions, offering better adaptability. This approach adheres to the fundamental equilibrium principle of equal chemical potentials $\mu_i^G = \mu_i^L$, resulting in

$$\phi_i y_i p = \gamma_i x_i f_i^0$$

where x_i and y_i represent the molar fractions of a component



(a)

(b)

(c)

(d)

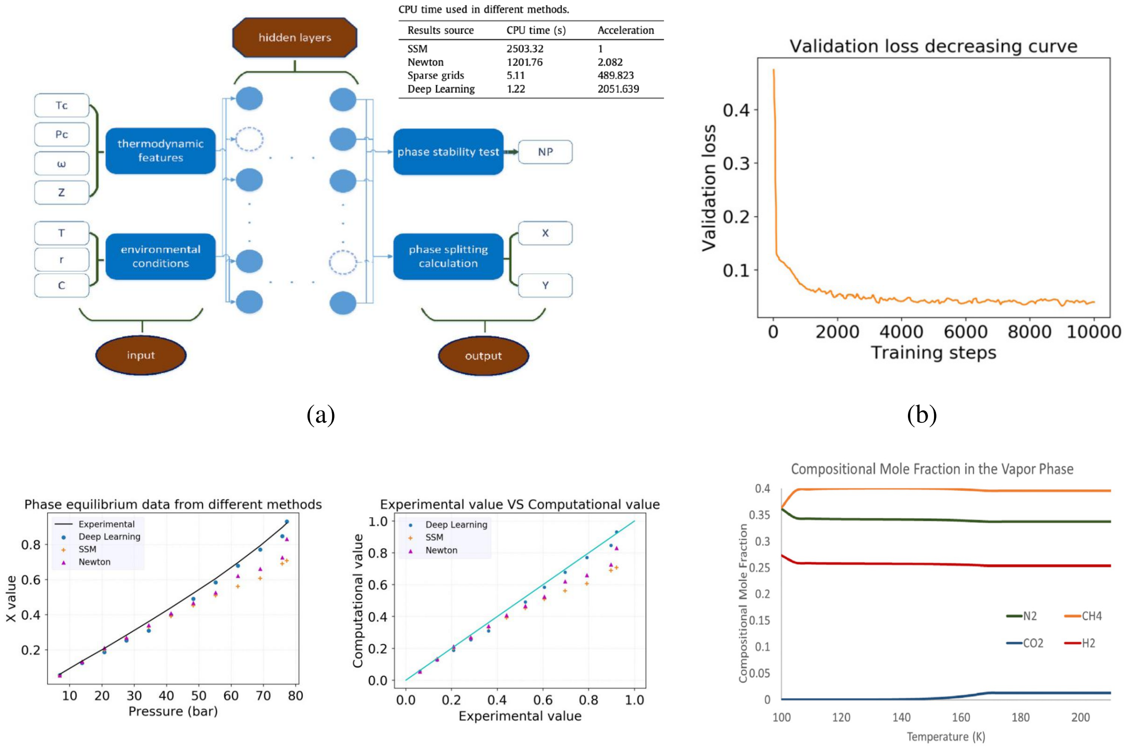
Fig. 6. Phase equilibrium diagrams of the H_2/N_2 mixture: (a) SR-RK and (b) PC-SAFT EoS with the phase identities (L, V and L+V), and critical points (Zhao et al., 2024); (c) the comparison on computational costs between one compositional simulator and one black oil simulator (Raad et al., 2023); (d) the 3D contour of tangent plane distance function of the $CH_4-CO_2-H_2$ mixture (Zhang et al., 2022).

in the liquid and gas phases, respectively, and γ_i is the activity coefficient of the solution, indicating deviations from the ideal solution.

Other progress includes: the solubility and water content tables have been generated using the electrolyte-PR-CPA model, along with a simple Setschenow-type formulation for quick and accurate calculations, and some new solubility data has been obtained using a volumetric method (Chabab et al., 2020; Chabab et al., 2024). The phase equilibrium challenges of $H_2 + CH_4$ brine mixtures in salt caverns are addressed using the parameterized electrolyte-polar PC-SAFT EoS, which is claimed to potentially offer accuracy in extrapolations due to its rigorous physical basis (Pinto et al., 2021). The EoSs designed for electrolyte demonstrates good adaptability to systems with brine and can be used to determine ion concentration through phase equilibrium calculation to evaluate the trend or rate of related geochemical reactions.

Another important issue with the phase equilibrium calculation is the huge computational costs since the flash calculations will be repeated in every step of compositional reservoir simulators when handling a dynamic flow simulation. It asks for some efficient algorithm to handle the trade-off between accuracy and efficiency. The traditional energy industry chooses black oil models with some simplification and bearing information loss. Even so, there is some work about UHS project modeling using commercial simulators using black oil (IMEX) and flash calculation (GEM) both. Recently, Raad et al. (2023) made some progress on extending the black oil model to the hydrogen-brine mixture in UHS by converting the equilibrium compositional data into the PVT data. They present the comparison of CPU time between the black-oil and compositional simulators, and a simple and efficient algorithm for this conversion is proposed and validated by experiment data as shown in Fig. 6(c). It also implies that the compositional simulator is time consuming.

With the explosion of machine learning technology, Artificial intelligence (AI) could potentially assist on this issue by training the prediction model offline one-time. Then it avoids the numerical computational time consumption associated with the flow simulation. Moreover, it can be continuously strengthened by online learning with more and more on-site data as the input. Zhang et al. (2020, 2024) proposed a thermodynamics-informed neural network (TINN) as shown in Fig. 7 to achieve an accelerating multi-component flash calculation process (Li et al., 2019), which not only boosts computational efficiency but also obeys the physical law since the training data is



CPU time used in different methods.

Results source	CPU time (s)	Acceleration
SSM	2503.32	1
Newton	1201.76	2.082
Sparse grids	5.11	489.823
Deep Learning	1.22	2051.639

(a) (b)

(c) (d)

Fig. 7. The information about TINN: (a) schematic of the thermodynamics-informed neural network (TINN) architecture and one table on its computational performance; (b) the profile of loss function with learning process in (Li et al., 2019); (c) the validation with experimental values; (d) one plot about the predicted partition of mixture containing hydrogen gas in (Zhang et al., 2024).

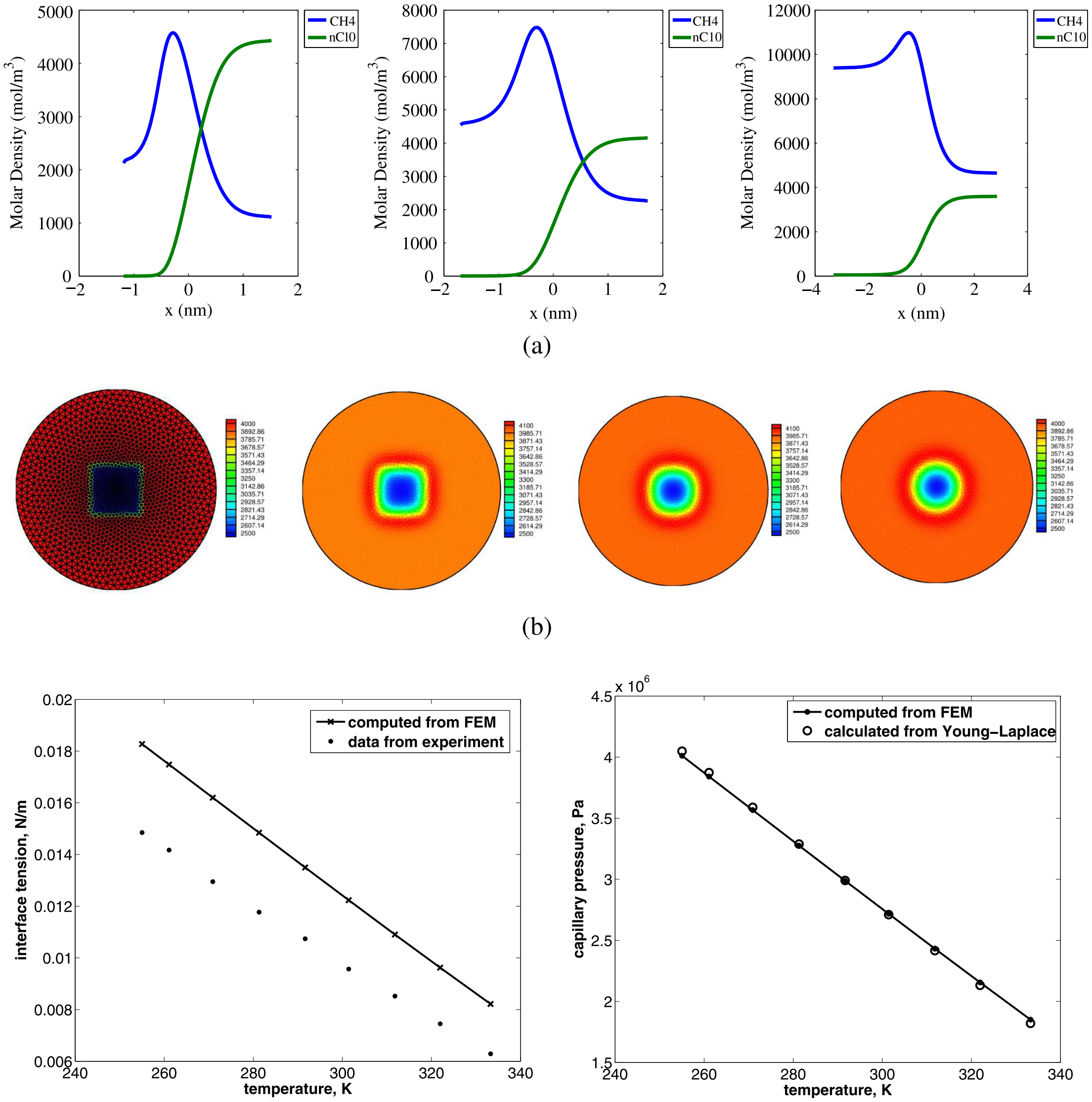
obtained by the thermodynamically consistent energy-stable flash calculation instead of using the limited experimental data. They apply this technique to investigate realistic fluid mixtures with hydrogen, and it accelerates the calculations nearly 20 times.

There is some other progress on how AI promotes phase equilibrium calculation or solubility simulation of UHS, including (Ansari et al., 2022; Tatar et al., 2022; Lv et al., 2024; Thanh et al., 2024). They use some machine learning tools, such as support vector regression, decision trees, or white-box techniques like genetic programming, to train the prediction models with an extensive data bank and validate them with a blind validation set. The results indicate that the results match the real physical trends of H_2 solubility change predicted by the cubic EoSs; some machine learning models outperform the cubic EoSs. The feature selection analysis also extracts the critical influence factors, which coincide with our physical knowledge. The vapor temperature, pressure, and salinity are also studied based on these machine learning methods or metaheuristic algorithms. Based on these results, we conclude that machine learning methods can play an important role and potentially assist our UHS exploration.

Furthermore, the underground hydrogen storage site could be in a shut-in state for a certain period of time, which necessitates the calculation of statistical phase equilibrium. Because it determines the steady state after a period of time and also gives a physically reasonable initial state for injection or extraction process prediction. It is worthy to remark that capillary trapping plays a crucial role in the storage of hydrogen in porous media underground; it not only affects recovery efficiency and storage capacity but also impacts hydrogen loss and the integrity of reservoir traps. Therefore, we should incorporate capillarity into our phase equilibrium calculation on the Darcy scale. Additionally, if future research explores the potential for storing hydrogen in shale reservoirs, this effect will be way more dominant. One possible way to incorporate capillarity is to use compositional grading modeling, which will be highlighted in the next section. The capillary pressure used in this compositional grading modeling at Darcy depends on the saturation and pore size distribution inputs, which can be obtained by upscaling the pore-scale modeling results. The pore-scale aspects will be mentioned in the following content.

3.2 Phase equilibrium with spatial information at pore scale

The spatial distribution and concentration variation of different components at the pore scale could influence the tendency of a geochemical reaction. Also, the concentration and transport of some nonlinearly sensitive factors, like the dissolved surfactant, can significantly influence interfacial



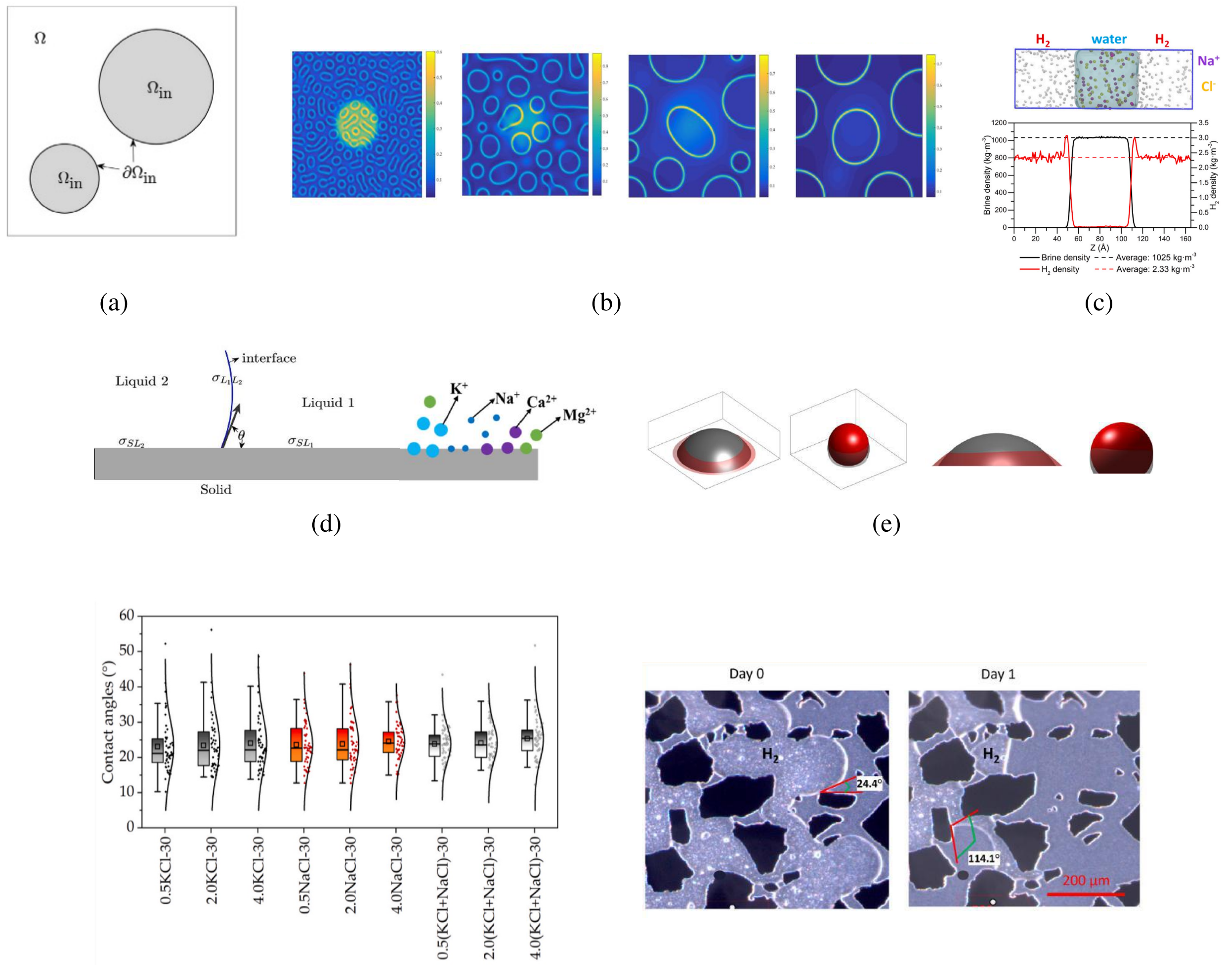
(a)

(b)

(c)

Fig. 8. Interface enrichment phenomenon reproduced by phase equilibrium modeling of the mixture CH_4-nC_{10} at the pore scale: the distribution of concentration evolves with time in (a) 1D and (b) 2D; (c) the interfacial tension calculation via numerical results and its validation with experimental data. (Kou et al., 2015; Fan et al., 2017; Qiao and Sun, 2014)

tension as well as wettability and contact angle at three-phase junctions. These factors, in turn, affect the drainage-imbibition process and the recovery efficiency of the entire UHS system at the Darcy scale. Therefore, the spatial information of the equilibrium problem at the pore scale is essential. It is observed that light components enrich at the interface region, reaching concentrations higher than those in the bulk phase. This physical phenomenon results from the difference in forces and interactions exerted on the light components by the gas and liquid phases. It might become more pronounced with the presence of hydrogen. The forces at the interface are not limited to Van der Waals forces; they may include hydrogen bonding, electrostatic forces among charged ions, and so on. Thus, this interfacial enrichment phenomenon occurs not only at the pore scale but also at the molecular scale, at gas-liquid interfaces but also at gas-solid or liquid-solid interfaces, as shown in Figs. 8(a), 8(b), 9(b) ,9(c) and 9(d). Thus, this kind of phenomenon broadly encompasses the aggregation of surfactant at the interface, the formation of electric double layers, and other important interfacial phenomena in UHS (Zhu et al., 2018; Choudhary et al., 2019; Zhu et al., 2019; Qiao et al., 2024). These phenomena, described by phase equilibrium theory, all arise from the minimization of energy. As we all knew, the hydrophobic interaction of surfactant is a typical entropy-driven phenomenon. Additionally, these interface enrichment phenomena have impacts on geochemical and biochemical reactions, resulting in biofilm formation, bacterial growth, channel clogging, and a decrease in permeability. They can also directly affect the wettability of H_2, as reported by Liu et al. (2023) in their study on microbial-induced wettability



(a) (b) (c)

(d) (e)

(f) (g)

Fig. 9. (a) The Schematic of two-phase interfaces; (b) the migration and enrichment of surfactant at the interface region (Zhu et al., 2018); (c) interfacial enrichment phenomenon at molecular scale (Medina et al., 2024); (d) the schematic of contact line problems with some common ions in the solid material; (e) the comparison on the contrary wettability (Zhu et al., 2019); (f) the contact angle of glass/H_2/brine for different brines and salinities (Medina et al., 2024); (g) the alteration of wettability caused by the bacterial (Liu et al., 2023).

alteration as shown in Fig. 9(g). Thus, it is essential to model and analyze phenomena like interfacial enrichment through phase equilibrium with spatial information at the pore scale.

In pore-scale research (Cui et al., 2022), the bulk phase and interface are two important parts of a phase equilibrium system. It is necessary to describe the interface morphology, find out how the components are distributed in space, and figure out important parameters like surface tension and capillary pressure. Currently, the methods to describe the interface mainly include three categories:

1) Using a specific inter-molecular potential function with molecular dynamics or molecular Monte Carlo methods (Yang et al., 2022).
2) The sharp interface method, based on geometric concepts like curvature, assumes a zero-thickness interface as a two-dimensional entity with jumping conditions between phases to describe interfacial tension (Sun and Tao, 2010).
3) The diffuse interface method, based on gradient theory or phase field theory, describes the interface as a continuum three-dimensional entity (Yang et al., 2022; Feng et al., 2023).

Based on the diffuse interface theory, the density, or order parameter, transitions smoothly over a finite region at the interface, and the concept of energy density provides ample physical details for the interface itself. Qiao and Sun (2014) first utilizes the gradient theory of thermodynamics and variational calculus to derive a generalized chemical equilibrium model. The model is based on Helmholtz free energy, where the free energy for the bulk phase includes both ideal and excess parts:

$$F_0(\mathbf{n},T,\Omega)=F_0^{\text{ideal}}(\mathbf{n};T,\Omega)+F_0^{\text{excess}}(\mathbf{n},T,\Omega)$$

where F_0 denotes the Helmholtz free energy of the homogeneous part and $\mathbf{n}$ denotes the molar density vector of one mixture. Given the concentration variation of components at the phase interface, based on gradient theory, there exists a mixing energy term, $F_\nabla(\mathbf{n};T,\Omega)$, to account for this part of energy. Therefore, for the entire system, the expression for free energy can be articulated as:

$$F(\mathbf{n};T,\Omega)=F_0(\mathbf{n};T,\Omega)+F_\nabla(\mathbf{n};T,\Omega)$$

The inhomogeneous term, F_∇ mixing energy contribution can be modeled by a simple quadratic relation:

$$f_\nabla(\mathbf{n})=\frac{1}{2}\sum_{i=1}^{M}\sum_{j=1}^{M}c_{ij}\nabla n_i\cdot\nabla n_j$$

where f is the energy density, i represents each component and c_{ij} is the influence parameter. Then we need to seek $\mathbf{n}\in H$ such that

$$F(\mathbf{n})=\min_{\widehat{\mathbf{n}}\in H}F(\widehat{\mathbf{n}})$$

Subject to $\int_\Omega \mathbf{n}d\mathbf{x}=\mathbf{N}$, the mass conservation constraint can be enforced by a Lagrange multiplier. The necessary conditions for the phase equilibrium state with respect to chemical potential, defined as the variational derivative:

$$\mu_i=\frac{\delta f(\mathbf{n})}{\delta n_i}=\mu_{0,i}+\mu_{\nabla,i}$$

With the aid of basic thermodynamic theory, it yields

$$-\sum_{j=1}^{M}c_{ij}\Delta n_j=\mu_i-\mu_{0,i}(\mathbf{n})$$

Then it can be converted into a time-dependent parabolic PDE, with our main interest in its final equilibrium state.

$$\frac{\partial n_i}{\partial t}-\sum_{j=1}^{M}c_{ij}\Delta n_j=\mu_i-\mu_{0,i}(\mathbf{n}(\mathbf{x},t))$$

Some energy-stable schemes can be designed to achieve unconditional convergence using convex-concave splitting methods or some others (Fan et al., 2017). Furthermore, the interface tension σ characterized by the net contractive force per unit length of interface, with a unit of N/m, can also be defined as the work for creating a unit area of interface, with a unit of J/m^2. Thus, the following equation can be used to approximate the surface tension at the equilibrium state:

$$\sigma=\frac{F(\mathbf{n})-F_0(\mathbf{n}_{\text{init}})}{A}$$

Or a more general definition (Kou and Sun, 2014):

$$\sigma(\mathbf{n})=\int_\Omega\left(\Phi(\mathbf{n})-\Phi_B+\frac{1}{2}\sum_{i,j=1}^{N}c_{ij}\nabla n_i\cdot\nabla n_j\right)d\mathbf{x}$$

where Φ denotes grand potential and $\Phi(\mathbf{n})=f_0(\mathbf{n})-\sum_{i=1}^{N}\mu_i n_i$, Φ_B is the value of Φ in the equilibrium state. $\Phi(\mathbf{n})$ is generally greater than Φ_B.

The interfacial tension is the crucial parameter for describing the capillary effects, wettability, drainage, and imbibition processes in UHS. From the numerical results computed by this diffuse interface model, the interfacial enrichment can be clearly observed from the concentration curves of the 1D problem and the contour fields of the 2D problem, as shown in Figs. 8(a) and 8(b). The interfacial tension and capillary pressure predicted through this numerical method agree very well with the experimental data as shown in Fig. 8(c). There are some similar interfacial phenomena that have been reported in the UHS research projects. It was reproduced by the molecular dynamic method, as shown in Fig. 9(c), where there is a marked increase in hydrogen concentration at the H_2-brine interface at molecular scale. which proves that this phenomenon occurs at the molecular scale as well. Medina et al. (2024) investigates H_2-brine systems, which are widespread in UHS systems. Their work not only reveals interfacial enrichment but also includes the estimation of interfacial tension (IFT) with varing ion types, salinity in brine and pressure, and the contact angle of H_2-brine-glass in micro-fluidic systems as Fig. 9(f) display. A thermodynamically consistent model with a contact line is also proposed based on this pore-scale phase equilibrium model (Zhu et al., 2019) as Figs. 9(b) and 9(e). Both the enrichment of surfactant and compositions are induced by the minimization of energy (entropy increase law); therefore, we conclude that thermodynamic consistency is very important for the design of mathematical models and numerical schemes.

There are some other progresses for the pore-scale research at the UHS. Song et al. (2023) found three pore-scale mechanisms via the micromodels: preferential-to-uniform flow transformation, floating flow, and dead-end pore invasion. Based on these mechanisms, they recommend that a brine-saturated initial condition with high injection flux and median pore heterogeneity is optimal for both UHS capacity and efficiency, which may potentially improve on-site decisions in future engineering applications. A coupled, pore-scale model governing the conversion of hydrogen to methane, such as advective hydrogen flow, its diffusion into microbial biofilms of multiple species, and its consumption within these biofilms is proposed by Ebigbo et al. (2013). They use this model to investigate the competition between three different microbial species: methanogens, acetogens, and acetotrophs. As we mentioned, the geochemical and biochemical reactions are vital for the UHS, and the results of this work show a significant impact, as we expected. This model paves a possible path to characterize this process.

Lysyy et al. (2022) use microfluidics to investigate the effect of capillary number on hydrogen saturations, displacement/trapping mechanisms, dissolution kinetics, and contact angle hysteresis experimentally. They found H_2 saturation after drainage increased with increasing capillary number; static and dynamic contact angles ranged from 17° to 56°, confirming the non-wetting hydrogen nature. Wang et al. (2023) investigated hydrogen transport in a pore network in a sandstone porous medium at strongly water-wet and weakly water-wet (hydrogen-wet) through the direct numerical simulation of volume of fluid (VOF) methods, which we also mentioned above as one of the classic sharp interface methods. The numerical results show that increasing hydrogen wetting has a decreased snap-off effect, enabling a greater pore space for hydrogen storage for the drainage process, During the imbibition process (hydrogen extraction), the wetting becomes unfavorable due to the stability of hydrogen clusters. Also, the high interfacial tension and low viscous force make the snap-off effect dominant for both processes, regardless of wetting conditions. Zhang et al. (2023) use high-resolution three-dimensional X-ray imaging to study the injection and withdrawal processes of H_2. They found a significant rearrangement of the trapped hydrogen 12 hours after imbibition. Many smaller ganglia disappeared while the larger ganglia swelled, with no detectable change in overall gas volume. But this phenomenon does not occur for N_2. They claim that the Oswald ripening is responsible for this rearrangement, and it is promoted by the concentration gradient of dissolved gases in the aqueous phase. Finally, it will lead to increased gas connectivity, less hysteresis, and more efficient withdrawal. Ostwald ripening is a typical phenomenon based on the principle of minimum system energy as well. The above experiments and numerical testing imply that energy is very important; it influences the interfacial and contact line phenomena directly and finally impacts the performance of UHS.

These aforementioned studies highlight the necessity of pore-scale experiments and numerical modeling in UHS projects, as well as the importance of thermodynamically consistent phase equilibrium calculations once again. Research at the Darcy-scale, pore-scale, or molecular level reveals that phase equilibrium processes play a critical role in the complex subsurface challenges of UHS. They are one of the decisive factors in determining phenomena spanning across scales and involving multi-physical mechanisms, including chemical reactions, rock mechanics, and so on. Continuous efforts and joint studies on phase equilibrium across various scales via more comprehensive experimental and numerical simulation are important directions to expedite the practical engineering implementation of UHS projects. Previous experience and scientific approaches in conventional natural gas underground storage or CO_2 sequestration can aid in the rapid development of UHS.

4. Hydrogen-induced mechanisms and effects

However, due to the unique properties of hydrogen, the UHS is not merely a transfer or copy of technology and management. Issues such as hydrogen embrittlement (HE) have long plagued all industries related to hydrogen. Furthermore, the properties of hydrogen make it prone to escape, difficult to detect once leaked, and have a wide explosive range, significantly increasing engineering risks. High-quality materials, high-standard storage geological conditions, advanced sealing and anti-corrosion technologies, and more thorough production and safety operation plans are required.

4.1 Hydrogen embrittlement

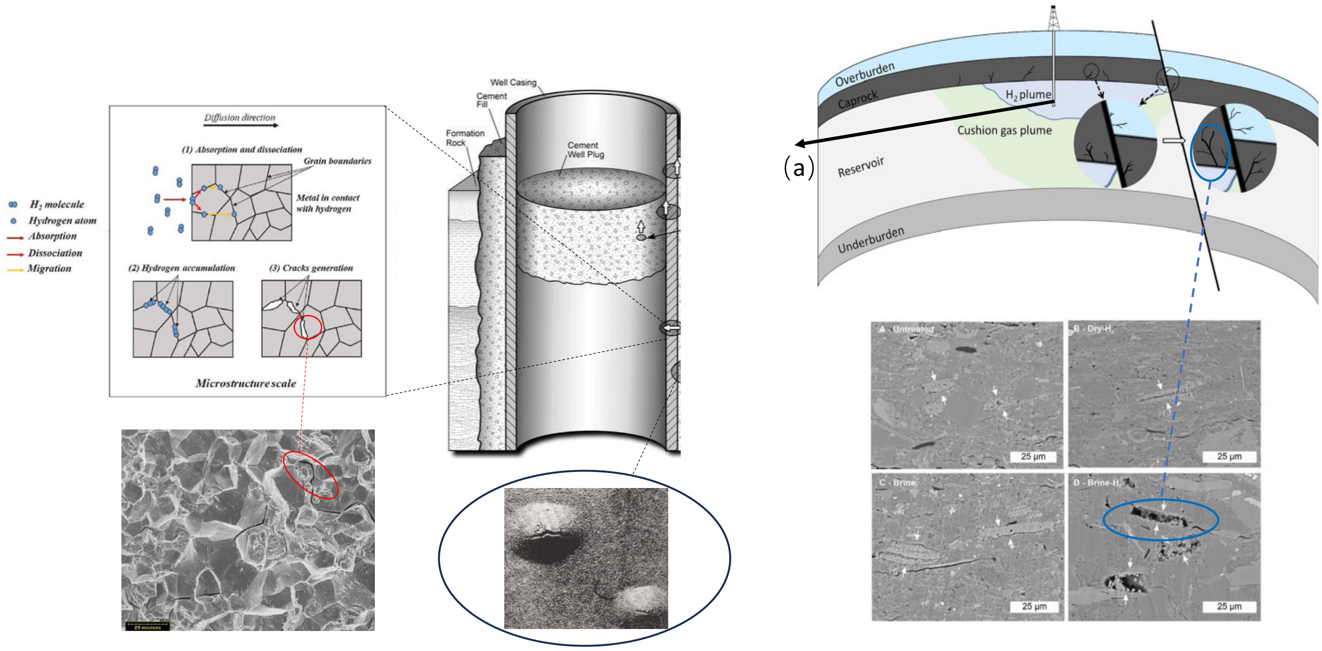
Hydrogen embrittlement generally refers to the process where hydrogen gas interacts with metals, leading to changes in metal stress and eventually resulting in brittle cracking as shown in Fig. 10(a). The main transport process consists of the following: (1) adsorption and dissociation of hydrogen molecules on the metal surface; (2) diffusion of dissociated atoms into the interior of the metal; and (3) movement and aggregation of atoms in the interstices of the metal lattice. The mechanisms leading to metal cracking include:

- Reduction of the resistance to dislocation movement (reducing plasticity, reversible HE)
- Promotion, occupation, and stabilization of vacancies (reducing plasticity, reversible HE)
- Weakening the bond between metal grains (increasing brittleness, reversible HE)
- Aggregation causing local high pressure in metal (stress concentration, irreversible HE)
- Formation of hydrides in alloys (phase change, irreversible HE)

These are critical mechanisms that trigger hydrogen embrittlement, and the related theories are still continuously being debated and refined. In engineering practice, material susceptibility, stress, and the environment are jointly responsible for the occurrence of hydrogen embrittlement. In the context of UHS, hydrogen embrittlement primarily impacts wellbore integrity. Components susceptible to corrosion include tubes, casing pipes, packers, wellheads, valves, and downhole pumps, among all metal parts. Moreover, hydrogen can interact with cement either through the well bottom or after permeating through the casing, ultimately leading to cement degradation and the formation of leakage paths. Additionally, geochemical or biochemical reactions producing acidic gases, such as H_2S or CO_2, may induce corrosion, thereby increasing the likelihood of hydrogen embrittlement. High concentrations and high pressures reduce the reducibility of metallic materials. Furthermore, the cyclical stress variations occurring during injection and extraction processes exacerbate these failure phenomena. In order to prevent long-term exposure of the wellbore to a hydrogen environment, especially when the storage facility is in a shut-in state, consideration can be given to replacing the gas segment between the bottomhole valve and the wellhead with N_2 gas. Other equipment should consider the use of materials such as low- and medium-carbon steel and corrosion-resistant alloys, while also employing strengthening methods such as coating with a film or surface modification. Factors like temperature, pressure, and hydrogen concentration may affect the severity of hydrogen-induced damage; thus, phase equilibrium calculations to determine the thermodynamic state and hydrogen concentration distribution along the wellbore can aid in corrosion protection and detection efforts. As shown in Fig. 10(b), not only the H_2-embrittlement for metal, but H_2 can alter the caprock and make some pathway to leak out and cause integrity failure of the trap itself, which will be mentioned in the following content.

4.2 Comparsion between CCUS and UHS

Aside from the unique phenomenon of hydrogen embrittlement, a comparison with CO_2 underground storage between H_2 and CO_2 storage, as shown in Fig. 11, is beneficial for identifying key points of the UHS. Regarding trapping mechanisms, both encompass the common four types: (1) structural trapping; (2) capillary trapping; (3) dissolution trapping; and (4) mineral trapping. Usually, CO_2 sequestration is aimed at long-term, even permanent storage, making the latter two mechanisms more preferred in CCUS as the high solubility of



(a) (b)

Fig. 10. The integrity problems caused by hydrogen-induced alteration or cracking: (a) H_2 embrittlement of metal equipment (Celia et al., 2005; Fernandez et al., 2024); (b) the alteration of caprock (Bensing et al., 2022; Zeng et al., 2023)

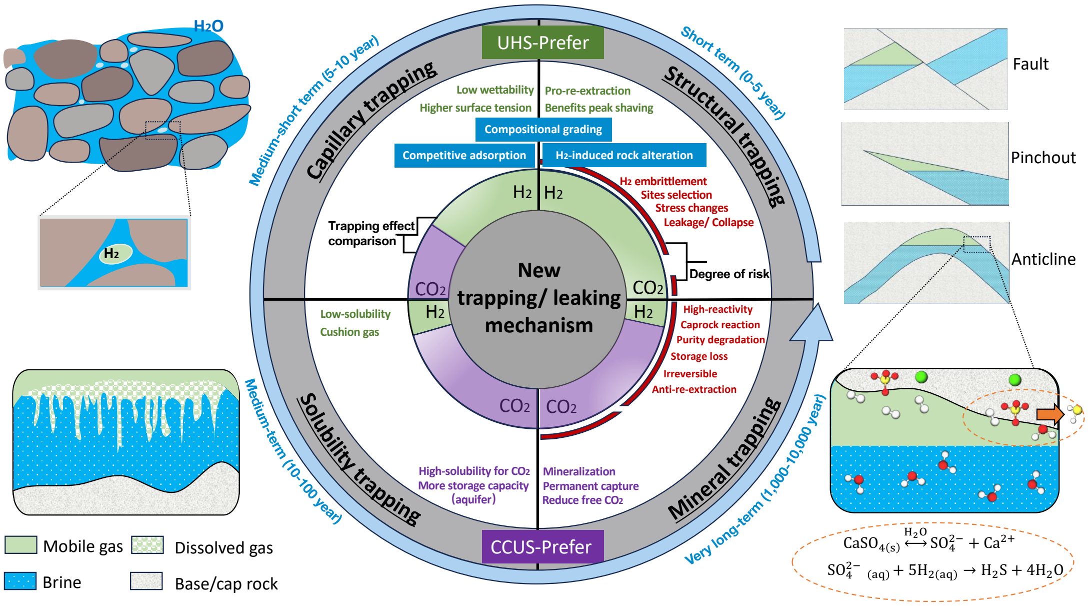


Fig. 11. The four trapping mechanisms, their time span of effectiveness in CCUS/UHS and comparisons of their preferences and risks.

CO_2 in saline solutions significantly enhances storage capacity. Moreover, CO_2 can react with subsurface minerals, mineralizing carbon elements and transforming them into a solid state for permanent sequestration. In contrast, hydrogen is intended for temporary energy storage, necessitating retrieval at specific times, thus favoring the first two trapping mechanisms. The lower solubility of H_2 in saline, coupled with its inertness assuming the absence of catalysts, just meets our desired outcomes for energy storage. Therefore, the underground storage environment naturally presents many advantages for both CCUS and UHS; we must take advantage of them. However, the potential for hydrogen loss due to chemical reactions with subsurface microbes or mineral dissolution, purity reduction, and issues like caprock sealing degradation have significantly negative effects. Compared to the CCUS, preventing geochemical and biochemical reactions becomes one of the most crucial concerns at the UHS. These chemical reaction issues are somewhat mitigated in salt caverns, where the high salinity environment naturally curtails most microbial activities. But the salt cavern has its own shortcomings, like a larger initial investment and a smaller storage scale compared to reservoirs.

Regarding the first two mechanisms, capillary trapping is primarily influenced by interfacial tension and wettability. Notably, assuming brine is the wetting phase, as in most cases reported in the above literature, during the injection/drainage phase, the interfacial tension causes more hydrogen to be trapped, effectively immobilizing it, and this may enhance storage quantity to some extent. While it also means the trapped hydrogen may not be easily retrievable at extraction/imbibition phase. Adding some additives for reproduction, such as surfactant or hydrogen foam, can increase the likelihood of contact between the flowing and trapped hydrogen, thus potentially enhancing retrieval. Therefore, from this perspective of mechanisms, researching pore-scale phase equilibrium with spatial considerations and models that involve surfactant enrichment at interfaces to reduce interfacial tension can play a critical role in improving the storage and recovery efficiency of UHS. However, regarding the seal integrity of the reservoir, if the caprock is wetting-type, then the liquid phase present in the caprock may aid in H_2 sequestration through interfacial tension, reducing the tendency of hydrogen passing through the caprock, which is also called capillary sealing.

Structural trapping, as the main trapping mechanism, accounts for the majority of the total storage capacity for both CO_2 and H_2. The volume involved in this part does not significantly differ between CO_2 and H_2 from a storage capacity perspective. However, due to the unique properties of hydrogen, the selection of geological sites determines whether H_2 storage can be compared with CO_2, as leakage loss will more or less always exist. Therefore, the main influencing factor for this part lies in the integrity of the trap, necessitating increased attention to the formation of leakage paths and changes in geomechanics. Nonetheless, due to its properties, hydrogen's gravity override, viscous fingering, and uncontrollable lateral expansion of the plume are undesirable, even for structural trapping, because they require more energy to recover a wider range of hydrogen gas and significantly impact its economic viability. Based on these four common trapping mechanisms, we want to highlight three other important mechanisms affecting UHS, which include: (1) compositional gradient; (2) competitive adsorption; and (3) hydrogen-induced rock alteration, as shown in Fig. 12.

4.3 Compositional grading

In previous discussions, we mentioned a series of gravity segregation phenomena caused by the hydrogen density characteristics. The distribution of compositions and thermodynamic properties of mixtures will directly determine flow pattern, trapping, and chemical reaction rates, and eventually affect recovery efficiency, purity, and storage safety. However, other factors like temperature and capillarity also significantly influence compositional grading. Thus, the concept of compositional grading will cover more factors, generalizing the mechanisms with good extensibility. We have discussed that the capillarity also affects the phase equilibrium at the Darcy scale; the model of compositional grading is just a remedy for considering spatial information. Sun (2019) proposed a computational framework for this composition based on Helmholtz free energy that includes additional energy terms and solves for energy minimization to achieve the equilibrium state, thus enabling the description of the spatial distribution of components at equilibrium. The magnitude of surface tension can be even linked to the distribution of pore sizes, better building up the connection between pore scale and Darcy scale.

By extracting the main characteristic directions on the Darcy scale, the computational effort can be significantly reduced. The results of compositional grading calculations can accurately predict the equilibrium state in UHS, such as the final state that an storage system can reach after a long shut-in period, and this steady state can also serve as a physically meaningful initial setting for dynamic production processes in one compositional simulator. Currently, research on compositional grading at UHS is limited. Zhou et al. (2024) proposed a model considering thermal and gravity-induced compositional grading of hydrogen-containing gas mixtures based on cubic EoS. They validated some of their results against data from NIST and H2Thermobank. The results demonstrated that the stratification tendency between cushion gas and H_2 is minimal and can be neglected in engineering. Under static storage conditions, H_2 and a natural gas cushion tend to mix into a rather homogeneous mixture, posing significant challenges for producing high-purity hydrogen. Compared to porous media, the cavity of a salt cavern is more prone to instability, and gas diffusion happens faster due to diffusion, making the mixing issue more severe. Similar conclusions have been validated in simulations of hydrogen-blending in pipelines and tanks (Su et al., 2024). Despite this, the compositional grading effect caused by capillarity in a tighter formation cannot be ignored.

4.4 Competitive adsorption

Competitive adsorption is another crucial mechanism in UHS, as it can benefit the sealing of caprock. Recently, Liu et al. (2024) in their study of the H_2 leakage problem using molecular dynamics (MD) and MD-Monte Carlo (MDMC) methods (Liu et al., 2022), discovered that caprock defects are repaired by H_2O clusters due to hydrogen bonding and the adsorption of H_2O on the caprock surface. Methane also forms an adsorption layer, which to some extent inhibits contact between H_2 and the rock face. With increasing temperatures, the evaporation of water leads to a degree of decay in molecular sealing. Smaller pore sizes (<10.0 Å), higher humidity in the atmosphere, and the presence of cushion gases like CH_4 can all influence sealing to some extent. They explains this competitive adsorption mechanism through their potential energy distributions and interaction forces. Ho et al. (2024) also conducted molecular simulations to study H_2/CH_4 adsorption and diffusion, investigating competitive adsorption and diffusion of H_2/CH_4 in kerogen, a common component of shale. There are two H_2 populations, i.e., free H_2 and adsorbed H_2. The simulation results also indicate that CH_4 outcompetes H_2 in adsorption onto kerogen, due to stronger CH_4-kerogen interactions than H_2-kerogen interactions. The results from MD show great consistency with the results from nuclear magnetic resonance (NMR).

4.5 Hydrogen-induced rock alteration

Similar to hydrogen embrittlement, hydrogen not only causes changes in the mechanical properties of metals but can also lead to hydrogen-induced rock alteration. Firstly, certain rocks inevitably contain metallic components and possess lattice interstices; therefore, the mechanisms of hydrogen embrittlement occurring in metals, such as stress concentration due to hydrogen diffusion within rocks, are also applicable to rocks. Secondly, rock surfaces typically have larger voids than metals, facilitating hydrogen migration. In underground environments, certain microorganisms can activate hydrogen reactivity, and related chemical reactions may reduce rock integrity. In the research by Bensing et al. (2022) experiments revealed hydrogen-induced calcite dissolution in Amaltheenton formation claystones. The potential calcite dissolution due to brine-H_2-rock interaction found in the experiment can affect the sealing integrity of UHS. Additionally, hydrogen infiltration can decrease strength and lead to operational complications in UHS systems subjected to cyclic pressure changes during injection or withdrawal. Therefore, in some cases, if the caprock is wet, it might counteract the sealing because it accelerates rock dissolution, and some possible geochemical reactions, such as sulfate reduction, are more likely to occur in the presence of water. Consequently, the selection of sites might need to focus on the rock composition of the caprock and consider a balance between capillary sealing and the tendency for chemical reactions. When it comes to the salt caverns, the creep property of salt rocks enables the walls of the caverns to self-adjust and repair minor cracks or defects under long-term pressure, thereby improving their adaptability to cyclical stress variations and fatigue to a certain degree. This attribute is particularly valuable for managing pressure fluctuations during the injection and extraction processes. However, given that the interior forms a large-scale cavity with limited structural support, there is a risk of collapse. Therefore, controlling the structural shape of the salt cavern during the initial dissolution phase is crucial.

5. Conclusion

The UHS exhibits significant potential for contributing to the world's energy transition. However, some technologies remain in their infancy, and the long-term effects of hydrogen in underground storage are not fully understood. Thus, more fundamental research and feasibility analysis, either numerically or experimentally, should be conducted. In this article, we have comprehensively reviewed the unique thermodynamic characteristics of hydrogen, analyzing the interplay between phase equilibrium and other key effects such as flow pattern, capillary trapping, wettability, and geochemical reactions for the fundamental mechanisms, as well as drainage, imbibition, purity, integrity, and recovery efficiency for the engineering concerns.

We emphasize the importance of phase equilibrium issues in UHS to attract more scientific research attention to this area. Compared to CO_2 sequestration, this paper analyzes the differences between the two, offering constructive scientific insights based on four common trapping mechanisms. Additionally, we highlight three significant mechanisms unique to UHS. Through review, we point out that multi-scale integrative studies in UHS facilitate mutual validation of fundamental research, which, in the context of limited UHS engineering sites and data, aids in advancing related developments and reducing uncertainties in engineering practices. We also highlight many interesting and important mechanisms, such as gravity segregation, interfacial enrichment, competitive adsorption, and capillary sealing, where energy remains the most crucial determining factor across different scales. Therefore, from the perspective of mathematical modeling and numerical methods, ensuring thermodynamic consistency and the ability to inherit this property at the discrete level reflect the reliability and numerical robustness of simulation studies.

Recently, based on the fundamental laws of thermodynamics, specifically the principle of energy minimization (entropy increase), some elegant thermodynamically consistent models for addressing problems from zero-dimensional to 1D, 2D, and 3D across different scales (Darcy-scale, pore-scale, even atom scale) have been proposed. These models include phase equilibrium with capillary pressure (zero-dimensional), the compositional grading models (1D), partially miscible diffuse interface models, pore-scale flow models with surfactant, and multi-phase Darcy flow models (2D & 3D). Tailored to their unique mathematical characteristics, some energy-stable numerical simulation methods have been developed based on various spatial discretizations (both mesh-based and mesh-free) and temporal discretizations accordingly. This suite of mathematical models and numerical algorithms is particularly suitable for addressing UHS issues, meeting the need for extensive numerical simulation validation, and integrating research across scales to reduce uncertainties in engineering applications. Thus, extending these methods to study specific fundamental mechanisms or engineering problems at UHS is highly encouraged.

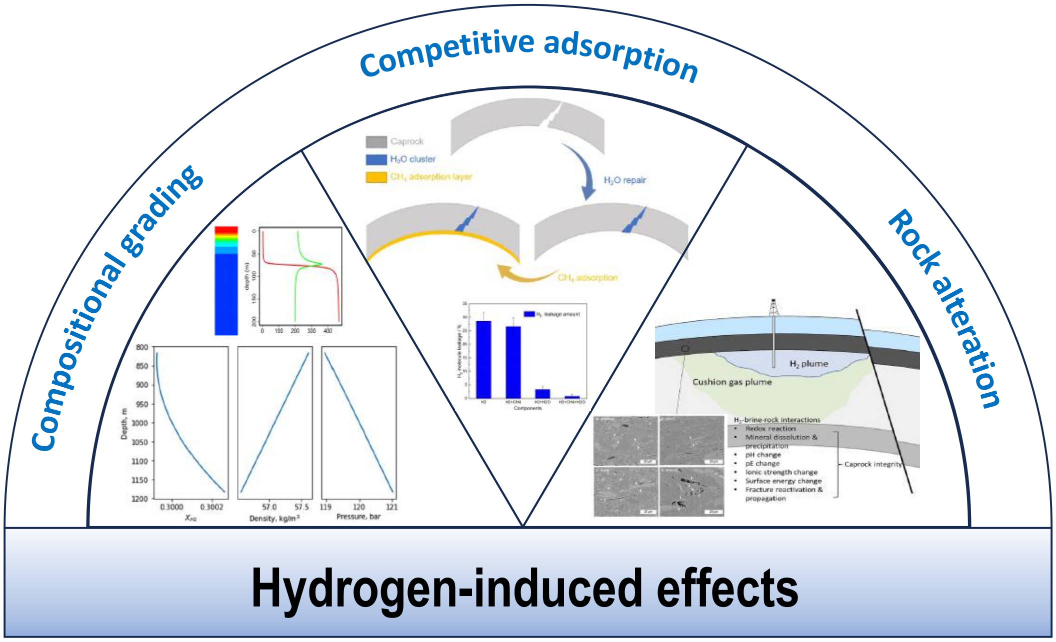


Fig. 12. Three highlighted hydrogen-induced effects in this paper (adapted from Zhou et al. (2024), Su et al., 2024, Liu et al., 2024, Bensing et al. (2022), Zeng et al. (2023)).

Nomenclature

AGA = American Gas Association
GERG = Groupe Européen de Recherches Gazières
NTP = normal pressure and temperature
NRTL = Non-random two-liquid model
SRK = Soave-Redlich-Kwong
SR-RK = Schwartzentruber-Renon-RedlichKwong
UNIQUAC = universal quasichemical

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Conflict of interest

The authors declare no competing interest.

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