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Perspectives and prospects of underground hydrogen storage and natural hydrogen

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Hydrogen is considered the fuel of the future due to its cleaner nature compared to methane and gasoline. Therefore, renewable hydrogen production technologies and long-term, affordable, and safe storage have recently attracted significant research interest. However, natural underground hydrogen production and storage have received scant attention in the literature despite its great potential. As such, the associated formation mechanisms, geological locations and future applications remain relatively under-explored, thereby requiring further investigation. In this review, the global natural hydrogen formation along with reaction mechanisms (*i.e.*, metamorphic processes, pyritization and serpentinization reactions) as well as the suitable geological locations (*i.e.*, ophiolites, organic-rich sediments, fault zones, igneous rocks, crystalline basements, salt bearing strata, and hydrocarbon-bearing basins) are discussed. Moreover, the underground hydrogen storage mechanisms are detailed and compared with underground natural gas and CO_2 storage. Techno-economic analyses of large-scale underground hydrogen storage are presented along with the current challenges and future directions.

1. Introduction

The demand for hydrogen has increased tremendously recently due to its application in several industries. Hydrogen can mainly be used in heavy oil and conventional petroleum upgrading, ammonia production, hydrogenation, metallurgical industries and hydrodesulfurization.[1] Additionally, hydrogen is preferred as an energy carrier and a promising alternative as sustainable fuel due to its renewability and environmentally friendly properties. Moreover, the combustion of hydrogen releases water vapour, and its mass calorific value (141.9 kJ g^{-1}) is three times higher than that of gasoline (47 kJ g^{-1}) and 2.6 times greater than that of natural gas (54 kJ g^{-1}).[2] Compared with other fuels such as ethanol and natural gas, hydrogen is

lighter.[3] On the other hand, the volume calorific values for hydrogen, gasoline and natural gas are 12.7, 34.2 and 40.6 MJ m^{-3}, respectively. Thus, more space is required to store the same amount of energy as gasoline or natural gas. Although the energy required to produce hydrogen can be higher than its energy yield, it is still considered an efficient energy carrier.[4–6]

Despite being promising, hydrogen faces several challenges in production and storage.[3] Significant quantities of hydrogen produced today are from steam methane reforming of natural gas.[7] A process that is not environmentally benign and generates tons of greenhouse gases. Moreover, hydrogen can also be produced from renewable sources such as biomass gasification,[8] water splitting,[9] dark fermentation,[10] and the water–shift reactions in syngas fermentation processes.[11]

As noted earlier, storing hydrogen cheaply and safely is very difficult. Additionally, the onboard hydrogen storage in vehicles is another bottleneck because of the stringent requirements in its storage. Currently, hydrogen is primarily stored in the gaseous or liquid form in pressurized or cryogenic tanks.[12] However, these technologies are insufficient to meet the requirements of large-scale storage. Therefore, there is a need to develop cost-effective, reliable, and safe storage systems to foster the development of a hydrogen economy. For broader context, the pros and cons of surface and subsurface hydrogen storage methods in practice are elucidated in Table 1. However, surface storage technologies are beyond the scope of this present work.

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Table 1 An overview of the advantages and disadvantages of subsurface and surface hydrogen storage technologies

	Underground hydrogen storage[5,13–18]	Compressed gas storage[19]	Liquid hydrogen storage[19]	Metal hydride-based storage[19]	Carbon-based storage[19]	Shallow-depth buried pipe storage[20,21]
Pros	Lower fire risk factors	Matured, established, and low-cost technology	Matured, established, and low-cost technology	Solid-state storage is characterized by good design flexibility	Lightweight, low-cost, and affords high storage density	Minimal contaminants/ impurities will accumulate in the stored hydrogen during standard operations
	High energy density: 250 W h L^{-1} It can last up to 50 years	It can last up to 20 years		They are typically considered safe	Intermediate energy density: 125 W h L^{-1}	It can last up to 50 years
Cons	Risk of hydrogen-consuming reactions and damage to the storage infrastructure under certain conditions	Limited capacity at typical operational pressures	It can be expensive	Relatively high-cost technology	Still in technological infancy	The maximum pressure is ~100 bar. Shallow depths limit them
	Still in technological infancy	Low energy density: 85 W h L^{-1} Further development is still required to advance high-pressure (>700 bar) storage. Existing technology is relatively expensive	High risk of hydrogen loss Liquid hydrogen production is energy intensive	Requires cooling circuit during filling Not lightweight and can degrade over time	Must be developed to improve reversibility and discharge rates	Highly susceptible to thermal expansion effects during injection and withdrawal, increasing the risk of structural damage[20]

Underground hydrogen storage in geological formations could be a cheap and environmentally friendly medium- and long-term storage route. Hydrogen can be stored underground in different layers such as aquifers, porous rocks, and salt caverns.[22] It should be mentioned that salt caverns do not exist naturally. Instead, they are artificial cavities in underground salt formations, that are created by the controlled dissolution of rock salt through water injection during the solution mining process.[23] Although underground hydrogen storage is similar to natural gas storage and has been demonstrated in salt caverns in the USA and the UK, challenges such as the selection of geological structures, process hazards and economics, and legal and social implications could hinder its commercial application. These challenges have been well documented in a previous study by Tarkowski and Uliasz-Misiak.[24] In another study, the same authors reviewed the barriers hindering the large-scale utilization of underground hydrogen storage.[25] Factors such as increasing cost of CO_2 emission allowances and declining "green hydrogen" costs are critical considerations for large-scale implementation of underground hydrogen storage.

Natural H_2 has been discovered in many locations worldwide, including Oman, New Zealand, Russia, Philippines, Japan, China, and the Italian and French Western Alps[10,26–28]

(with a cumulative yearly emission rate of 23 Tg)[29]. Its occurrence has been investigated and surprisingly discovered in some continental wells in Mali,[30] during hydrocarbon exploration in Kansas,[31] and in subsurface rocks and mines.[32] H_2 seepages have also been realized in sedimentary basins in Russia,[33] Brazil[34] and near the San Andreas Fault in California.[35,36] If discoveries of natural H_2 accumulations are exploited, it holds considerable potential as a key element in the energy mix either as a chemical raw material or as an energy carrier/fuel for transport. Nikolaidis and Poullikkas[37] demonstrated that all current methods of H_2 production are still too expensive to compete with fossil fuels favourably. Thus, natural H_2 discovery will likely yield a cost-effective improvement to the hydrogen economy. Moreover, combining natural H_2 discovery with underground storage could help mitigate the challenges of H_2 production and storage.

Several studies have reported the prospects and possibilities of storing hydrogen in underground formations.[5,38,39] Panfilov et al.[38] outlined the technical challenges of underground hydrogen storage. Tarkowski[39] presented the possibility of storing hydrogen in underground deposits in Poland. In another study, the mechanisms of underground hydrogen storage and the process feasibility were comprehensively

documented.[4] Despite the prevalence of underground H_2 storage in literature, a comprehensive review that comparatively discusses the prospects of artificially stored and naturally-occurring hydrogen is scarce. The present study provides a complementary overview of the necessary deployment and formation mechanisms involved in both scenarios, with insights into exploring and extracting this vital resource. It is hoped that the provided recommendations provided herein will not only inform researchers on the knowledge gaps to focus on in the coming years but also guide future large-scale investments in these technologies.

2. Underground hydrogen storage in geological structures

Underground hydrogen storage (UHS) is a promising route to addressing the demand-supply gap caused by the characteristic fluctuations of renewable energies. By exploiting the high specific energy (i.e., stored energy by mass) of hydrogen, the surplus generated energy can be readily converted to hydrogen and stored underground as a buffer for subsequent surges in demand.[4] Additionally, the UHS concept can offer additional safety advantages with respect to conventional supra-surface storage alternatives because it limits contact of the stored hydrogen with atmospheric oxygen (for example, in aquifers).[4,5]

Robust global technology road-mapping efforts highlight the potentials of UHS for addressing global energy- and emissions-related challenges.[14,40] Further demonstrating the timeliness and relevance of UHS technology is the fact that several projects over the last decade (e.g., H2STORE,[41–43] HYSTOREPORT,[16,17,44] HyUnder,[45] InSpEE[46–49] and HyINTEGER[50]) have focused on investigating different aspects of geological hydrogen gas storage and utilization. Moreover, it has been suggested that the reliability and cost-effectiveness of global energy systems should have improved sufficiently by 2050 to facilitate 17–22 TW h of annual subsurface hydrogen storage.[51]

While the properties of hydrogen as a gas in its pure state are more or less understood, hydrogen within multiphase systems such as in porous media is highly complex and is still in research infancy.[17] Moreover, the effects of robustness under cyclic loading and overall reversibility have been shown by Pfeiffer and Bauer[52] by using simulations of porous media hydrogen storage that under optimal conditions, extraction rates do not attenuate over four consecutive cycles. The authors remarked that further improvements in storage performance could be realized by adopting an optimized injection scheme to decrease the pressure levels, improving well injectivity. The importance of geological models cannot be understated.

In recent years, depleted gas/oil reservoirs, aquifers, and artificial underground cavities (such as salt and rock caverns) have been the subject of research attention for UHS.[4–6,17,39] These geologic formations have attractive attributes, which include but are not limited to: (i) good gas tightness; (ii) high wall (sealing) thicknesses compared to tanks for conventional storage; and (iii) extensive subsurface depths, which can minimize the risks posed to safety.

It is worth noting that UHS can benefit from the technological maturity of the geologic storage of natural gas and CO_2, which are associated with decades of established knowledge. However, H_2 is invariably more chemically, biologically, and microbially reactive, which presents unique challenges that are yet to be fully understood.[4,14]

Compared with natural gas storage, hydrogen storage in porous media (either aquifers or depleted reservoirs) similarly requires suitable geological structures such as well confined porous and permeable formations bounded by impermeable cap rock or seal to accommodate (accumulate) hydrogen safely at minimal losses.[4,53] Apart from the differences in the extraction (withdrawal) frequency of the gas, which is frequent in the case of hydrogen storage, most of the existing knowledge of hydrogen storage, especially in underground systems, has been learned from the natural gas storage experiences despite the different physiochemical properties of hydrogen in comparison with natural gases.[4] Leakage issues and loss of hydrogen are more common and severe in UHS than in natural gas storage (NGS) due to the lower density, viscosity, and molecule size of hydrogen.[54] In comparison to natural gas, the flow rate of hydrogen should be higher to avoid diffusion in porous media because of its lower viscosity and increased mobility. Wellbore of larger size may mitigate this issue.[4,54]

Similarly, carbon-geo storage (CGS)) requires the injection of CO_2 into porous geological formations located at least 800 m under the Earth's surface to realize pressures and temperatures to attain a liquid or supercritical phase.[55,56] At the CO_2 storage site, CO_2 is injected under pressure into the geological formation and once injected, it moves up through the storage site until it reaches an impermeable layer of rock called cap rock, overlaying the storage site, which traps the carbon dioxide in the storage formation. This storage mechanism is called "structural storage". It is the primary storage mechanism equivalent to the same process that has kept oil and natural gas securely trapped under the ground for millions of years.[55,57,58]

However, from the literature, a higher amount of CO_2 can be stored in the same structural volume compared to hydrogen.[57,59] CO_2 storage is intended to be a long-term and permanent storage known as CO_2 sequestration. The CO_2 storage operation is not cyclic, due to the characteristic absence of the withdrawal stage to meet the main goals of CO_2 storage – its removal from the atmosphere.[56,59] The co-production of CO_2 with other existing fluids in the porous media is not a concern in the case of CO_2 storage; besides, the problems such as withdrawal rates, number of cycles, and idle time between injection/withdrawal, are not encountered in CGS operation. Unlike UHS, different aspects of leakage risks from the caprock and operation facilities, and other failures resulting from corrosion need to be considered, in the case of CGS. More so, CO_2 is prone to reactions with rock and in situ fluids that promote the dissolution of the caprock minerals, further increasing the risk of leakage.[60,61]

According to Pan et al.,[59] the benchmark data from CGS and NGS projects are more often used to estimate or predict the behaviours of H_2 or the occurrences in underground hydrogen storage (UHS) reservoirs. However, relying entirely on such

a benchmark may be misleading since CO_2, H_2, CH_4 and other hydrocarbon fluids exhibit different physical and chemical properties.[59] Although it is an economic requirement to compare the existing data to assess any means of meaningful extrapolations and avoid serious pitfalls, it should be noted that only solid properties such as absolute permeability (K_a) and effective porosity (ϕ_{eff}) show a consistent trend among NGS, CGS and UHS. Fluid properties such as density (ρ), viscosity (μ), and fluid–fluid interfacial tension (γ_{FF}), and solid–fluid interactions such as capillary pressure (P_c), relative permeability (K_r), mobility ratio (M), adsorption–desorption and chemical reactions are significantly different. These differences imply that conclusions drawn from CGS and NGS reservoirs cannot be used directly in UHS.[62–64] Knowing that there are some subtle differences, as stated, calls for more detailed studies on the possible impacts and economic viability before embarking on UHS projects. Fig. 1 is a schematic representation showing NGS, CGS and UHS.

Typically, the process requires the pre-injection of cushion gas (*e.g.*, nitrogen or methane) before H_2 injection. Cushion gas can readily expand and be compressed during injection and extraction cycles to maintain the desired hydrogen pressures and flow rates without being consumed. As such, it constitutes a critical part of subsurface H_2 storage.[4] Already, its importance has been demonstrated for natural gas storage, where methane

as the working gas can be injected and utilized without the extraction of cushion gas, which is maintained to provide pressure support.[55]

Since natural gas is denser than hydrogen; the storage of hydrogen gas of the same mass requires more pressure, which in turn influences the storage capacity.[69] However, a higher amount of CO_2 can be stored in the same underground storage site compared to hydrogen because of its density, compressibility, and solubility.[13,56] A lower amount of H_2 can be stored in caverns, aquifers and depleted reservoirs than CO_2. As hydrogen is less dense than natural gas, the storage of hydrogen gas of the same mass often requires more pressure. This point raises the importance of storage capacity during a hydrogen storage operation.[13,69] Given the storage efficiencies of the NGS, CGS and UHS processes, a comparative overview based on location suitability, leakages, *in situ* reactions, displacement dynamics, water production during extraction, contaminants or purity issues, environmental issues, and costs is presented in Table 2. The interested reader may also consult the studies of Tarkowski *et al.*[39,56,57,70] for a more elaborate comparison.

2.1. Mechanisms

The primary mechanisms by which UHS can be realized are believed to be associated with diverse phenomena, including hydrodynamics, geochemical, physiochemical, biochemical
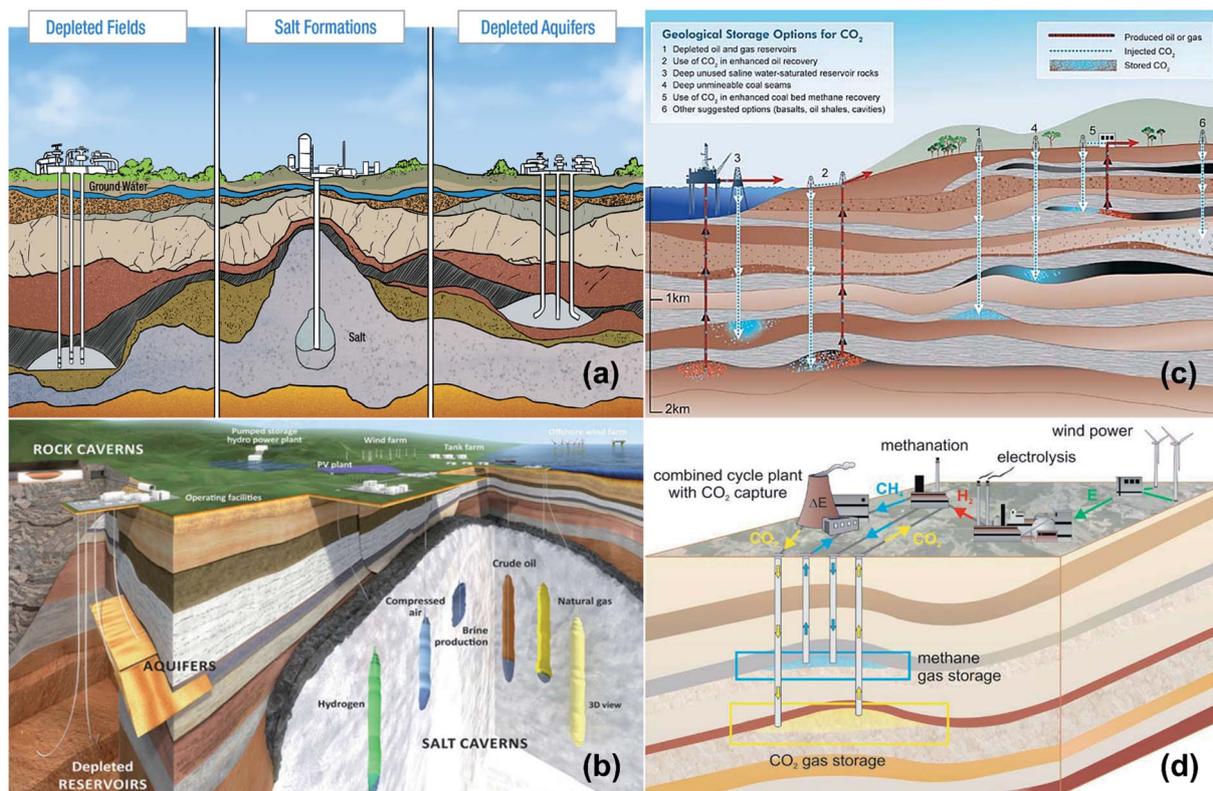

Fig. 1 Illustrations of viable geologic formations and schematic representations for (a) general underground storage of various substances (including H_2) in depleted hydrocarbon deposits, salt formations and aquifers;[65] (b) natural gas, liquid hydrocarbons, compressed air, hydrogen, and brine storage in salt caverns (showing cross-section through a salt dome);[66] (c) carbon geo-storage (CGS);[58,67] (d) integrated CO_2 and CH_4 storage.[68]

Table 2 Comparison of the storage efficiency concerns in NGS, CGS and UHS operations

Factors	Natural gas storage (NGS)	Carbon geo-storage (CGS)	Underground hydrogen storage (UHS)
Types of underground storage options	Depleted gas/oil reservoirs, aquifers, and salt caverns[56]	Depleted gas/oil reservoirs, aquifers, and salt caverns[56]	Depleted gas/oil reservoirs, aquifers, and salt caverns[14,56]
Storage adequacy	Caverns: favourable[71,72] Aquifers: least favourable[71,72] Depleted reservoirs: very favourable (Fig. 2)[71,72]	Caverns: favourable[73,74] Aquifers: very favourable[73,74] Depleted reservoirs: favourable[73,74]	Caverns: very favourable[75,76] Aquifers: least favourable[75,76] Depleted reservoirs: favourable[75,76]
Location suitability	Some restrictions in geographical locations for storage options[6,69,77]	There are fewer restrictions on geographical locations for all storage options[6]	Restrictions in geographical locations and capacity exist for cavern storage[69]
Leakages	Problems of leakage are minimized due to its high molecular weight, and high density making it less diffusive through overburden layers as compared to hydrogen[78,79]	CO_2 is more viscous and denser than H_2; hence may experience less leakage. However, the risk of corrosion of the downhole facilities when they are in contact with CO_2 (corrosive in nature) can increase the possibility of subsequent failures and consequent leakage[78,79]	Leakage of hydrogen to the surface is likely to happen due to its low molecular weight and low density, making it highly diffusive through overburden layers as compared to CO_2, or CH_4. Additionally, H_2 embrittlement may ensue in wellbore casings, causing corrosion and leading to further leakages[78,79]
In situ reactions	Fewer reactions with *in situ* fluids[15]	CO_2 often reacts with rock and *in situ* fluids that promote the dissolution of the caprock minerals, which further increases the risk of leakage[38]	Biochemical reactions can be considerably challenging for porous rock UHS, particularly where sulfate-reducing bacteria, methanogens and homoactogens are prevalent[15,38,44,80]
Displacement dynamics	Experiences less hydrodynamic displacement due to high density and low mobility compared to H_2 (ref. 53)	More viscous and low mobility relative to H_2 (ref. 53)	Low viscosity and high mobility, which lead to unusual hydrodynamic (unfavourable displacement) behavior such as fingering, gas rising, and overriding[53]
Water production during extraction	There is a relatively low occurrence of the water-coning phenomenon. This occurs when water overrides gas and breaks through the production well due to the dominance of viscous forces over gravity force in the reservoir – happening above a critical extraction rate[70]	There is a relatively low occurrence of water-coning phenomenon due to the dominance of viscous force over gravity force in the reservoir happening above a critical extraction rate[70]	There is significant water production during hydrogen extraction from porous rocks. The amount of hydrogen extraction and associated water production increase with flow rate[70]
Contaminants or purity issues	There are many pure methane storage projects both in porous formations and in salt caverns; however, practical experience with pure hydrogen storage is still limited[81]	There are already well-established pure CGS facilities given that CGS has attained a relatively advanced stage of development[70]	Most UHS projects are operated with mixtures of other gases. There are limited pure UHS facilities. The presence of impurities may hamper the feasibility and economy of the withdrawal stages and should be removed from the withdrawn gas stream[52,70]
Cost and economic viability	Minimal cost compared to CGS[56,58]	In addition to the capital, operational, *etc.* costs, corrosion inhibitory and leakage control costs usually add up to increase the cost of CGS compared to UHS[58]	Moderate storage costs compared to CGS and NGS.[58] Although further studies are required to assess the economic viability of the process
Environmental issues	Less environmental issues[58]	Environmental corrosion of the downhole facilities and other materials in contact with CO_2 (ref. 58)	No insurmountable or environmental problems with the storage of hydrogen in naturally formed underground structures[58]

Fig. 2 Volumes of different media require to store 100 TW h of H_2 energy. The equivalent H_2 storage volume of 1 depleted reservoir is 388 salt caverns.[72]

and microbial reactions.[4,6,38] Thus, further research and development in the area of UHS require a detailed understanding of the mechanism involved over time and with operational cycles.[4]

Presently, some of the main challenges limiting the advancement of the UHS concept are linked with hydrogen flow behaviour in reservoirs, understanding geochemical reactions occurring during and after the injection process, microbial hydrogen-consuming interactions, and of course, the implications of storage on the geomechanical characteristics of the formation under consideration. Other major bottlenecks stem from restricted locations, limited capacity, and assuring tightness in geological formations.[4,40] Ultimately, the applicability and development potentials of the UHS concept are dependent on the properties of the geologic structure.

Owing to this reactivity, toxic and corrosive gases can form. These can have deleterious effects on the wellbore, soil and atmosphere[14] and are thus, particularly important when considering the sustainability of UHS systems and the longevity of well materials.[14,51,82] For rock caverns, auxiliary components such as lining, pipework and compressors are often steel-based and can be compromised due to the inherent vulnerability of steel to hydrogen-induced embrittlement.[80] Moreover, identifying the condition-specific susceptibilities of specific sites to hydrogen consumption *via* sulfate reduction, methanogenesis and homoacetogenesis cannot be undermined.[44] Some of the most commonly encountered classes of microorganisms can consume up to 4533 nM hour^{-1} of hydrogen.[17] Thus, site selection is a precarious exercise to account for these factors,

often necessitating retrofitting exercises in the case of existing rock cavern storage sites,[80] and avoiding sulfate-, carbonate-, and sulfide-rich geological formations, which are typically undesirable for UHS.[14,15] Conversely, iron-rich formations should ideally be favoured.[15]

In terms of microbial interactions, many factors are still relatively unexplored and not fully understood; as such, more studies are needed, focusing on the development of robust predictive methods for microbial proliferation and hydrogen consumption across a broad range of geological hydrogen storage systems. Notably, more work on determining critical conditions (salinity, temperatures, pressures, *etc.*) can be highly insightful from a microbial interaction perspective.[44] Nonetheless, some early works in this regard have shown that methanogens, sulfate reducers, homoacetogens and iron(III)-reducing bacteria all have optimum pH of 6–7.5. For the same microorganisms, optimum salinities are <60, <100, <40 and <40 g L^{-1},
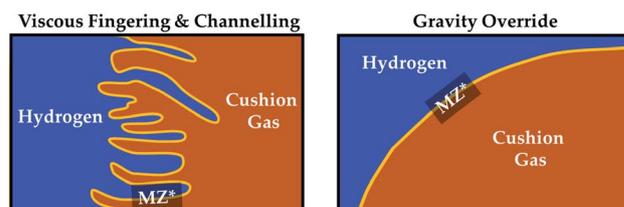

Fig. 3 Graphical illustrations of viscous fingering and gravity override phenomena. Note: MZ* indicates the mixing zone. Reproduced from ref. 16.

respectively. Finally, the optimum temperatures for sulfate reducers and homoacetogens are reported to be between 20–30 °C, while the ranges for methanogens and iron(III)-reducing bacteria are 30–40 °C and 0–30 °C, respectively.[17]

Owing to the low density and viscosity of hydrogen compared to other fluids, two unfavourable phenomena relate to the displacement efficiency during mixing upon injection. These are gravity override and viscous fingering (Fig. 3). Despite facilitating passive separation of the hydrogen gas from denser fluids such as cushion gas, the former can cause an accumulation of hydrogen gas above denser fluids (*e.g.*, in aquifers), which renders it vulnerable to losses.[16] The latter, which mainly occurs in the presence of native and cushion gases, can cause the hydrogen gas to extend beyond the desired displacement envelope of the well (typically anticlinal) and amplify other loss mechanisms. It is worth noting that in porous storage media, the low viscosity of hydrogen can favourably facilitate mobility and mixing.[16,83] Ultimately, strategic injection methodologies can effectively yield stable displacement for UHS to address these physical issues.[84,85]

Hassanpouryouzband *et al.*[16] remarked on the effects of changing temperatures and pressures within a reservoir on the mineral composition of formation fluids over time. A minuscule amount of hydrogen dissolution (into the fluids) can occur upon injection; with chemical disequilibrium, the hydrogen may become contaminated with water vapour. Residual trapping of a small fraction of hydrogen can take place, driven by capillary forces, and clay mineral surface adsorption can also occur. These events can trigger mineral dissolution and progressively compromise the reservoir and caprock tightness. At elevated temperatures and in the presence of hydrogen, adverse geochemical reactions can occur, releasing highly toxic gases and altering the pH of the water within the reservoir. This can exacerbate any ongoing mineralogic dissolution. This is closely supported by Heinemann *et al.*,[17] who suggests that hydrogen solubility in water can be significantly reduced under high-temperature and -salinity conditions, arguing that dissolved hydrogen does not directly affect the pH of the pore water.

Agreeing with previous studies, Hassanpouryouzband *et al.*[16] conclude that any mineral dissolution-driven reactions within the reservoir are, at best, indirectly affected by hydrogen with native chemical constituents of the formation fluids. These works highlight the complex interplay of the operational conditions and the formation geochemistry, warranting extensive exploration of hydrogeochemical interactions and effects for UHS. More importantly, both studies identify effused gases (*e.g.*, H_2S) from the aforementioned adverse reactions as key contaminants, which affect the quality of the stored hydrogen and induce unfavourable fluid–rock reactions; these constitute high risks from corrosion flammability and toxicity perspectives. This is also well supported by Hemme and Berk[15] who, by modelling the losses of hydrogen resulting from bacterial and hydrogeochemical interactions, identified that bacterial-driven losses were governed by the availability of co-injected CO_2 and native sulfate within the reservoir. Unsurprisingly, the authors also found a correlation between storage duration and loss, reporting a greater risk for hydrogen losses over more extended

storage periods. However, owing to higher co-injected CO_2 with successive injections, cumulative losses can be more significant due to a higher propensity for methanogenesis. The authors conclude that safer storage conditions can result after years of storage due to mineralogic attenuation over time with the consumption of anhydrite and calcite; bacterial sulfate reduction and methanogenesis are slowed due to the limited diffusion of sulfate and CO_2.

A qualitative overview of the comparative attributes of geological formations for UHS is presented in Table 3. Note that where values are reported for storage options that are yet to be proven or under investigation, the interested reader may refer to the cited literature for further details.

2.2. Important considerations

With the evolution of ongoing studies towards demonstrating the feasibility of the four main geologic hydrogen storage options, a myriad of critical factors must be considered, which may have wide-reaching implications on the future of UHS exploration and utilization. Thus, some of these vital considerations are summarised herein in addition to the review of research contributions in this area.

● Caglayan *et al.*[88] have argued that more attention should be paid to technical storage potential analysis and that land eligibility plays a massive role in the availability of viable sites for exploration. Stringent site exclusion criteria must be applied based on criteria such as proximity to urban and rural areas; major fault zones; land and transport infrastructure such as railway, major roads and gas pipelines; and natural protected areas and water bodies. Moreover, the authors demonstrate the importance of careful design and site specification, which must also account for geotechnical safety factors such as lithostatic pressure.

● Despite the marked favourability of salt caverns over other geological formations, the risk of hydrogen-consuming reactions can increase in the presence of thermophilic, salt-loving microbes.[75]

● However, the success of UHS in salt caverns will also chiefly depend on the availability of cavern-leaching water supply and appropriate brine disposal schemes.[5]

● Residual carbon-based species within depleted oil/gas reservoirs can have unfavourable interactions with stored H_2.

● Besides the criticality of the leak tightness of geological formations to their successful application, site-specific safety factors such as inherent susceptibility to seismic activities must be carefully assessed.[75] Additionally, site evaluations may require robust and accurate hazard predictions.[5]

● Limited availability of short-, mid-and long-term data may significantly inhibit site selection and performance assessment.

● Iron-rich formations can be considerably more beneficial, whereas sulfate-, carbonate-, and sulfide-rich formations should typically be avoided.

● As indicated in Table 3, while porous structures have specific dimensions, in the case of salt caverns, their volume depends primarily on the needs specified by the investor and the geological and mining conditions in the rock salt deposit.

Review

Table 3 Comparative overview of the main geological options for underground hydrogen storage. TRL: technology readiness level. Note, for site-specific attributes and/or storage options that are yet to be proven or under investigation, numerical values presented are indicative of ranges reported in the cited works. ★: poor; ★★: fair; ★★★: good; ★★★★: very good; ✈: site-specific; ↑: low; ↑↑: moderate; ↑↑↑: high

	Salt caverns	Rock caverns	Depleted reservoirs	Aquifers
Safety	★★★★[20,40]	★[20,40]	★[20,40]	★[20,40]
Gas tightness	★★★★[20,56]	★★[20]	★★★★[20,56]	★★[20,56]
Relative investment cost	↑[20]	↑↑↑[20]	↑[20]	↑[20]
Relative operational cost	↑[20]	↑[20]	↑↑[20]	↑[20]
Injection rate (kg h^{-1})	✈ ↑↑[20]	✈ ↑↑[20]	✈ ↑↑↑[20]	✈ ↑↑[20]
Withdrawal rates (kg h^{-1})	✈ ↑↑[20]	✈ ↑↑[20]	✈ ↑↑↑[20]	✈ ↑↑[20]
Working gas capacity/total gas capacity (%)	✈ ↑↑↑[80]	✈ ↑↑↑[80]	✈ ↑↑[80]	✈ ↑[80]
Feasible cycles per annum	↑↑↑[80]	↑↑↑[80]	↑[80]	↑[80]
Depth (m)	✈ 300–1800[20,80]	✈ 114–1000[20,80]	✈ 300–2700[20,80]	✈ 400–2300[20,80]
Operating pressure (bar)	✈ 35–270[20,80,86]	✈ 10–230[20,80]	✈ 15–285[20,80]	✈ 30–315[20,80]
Suitability for hydrogen	Proven,[80,87,88] TRL: 8 [80]	First UHS trial in development to be commissioned 2022,[80] TRL: 5–6 [80]	Still under investigation. Proven for town gas with up to 50% hydrogen,[80] TRL: 8 [80]	Proven for H$_2$–CH$_4$ blends with up to 10% H$_2$. Pure H$_2$ under investigation,[80] TRL: 3 [80,86]
Key factors & considerations	Salt domes are preferred over bedded salt formations	Metamorphic/igneous rock	Operational considerations; formation fluid and rock composite and microbial activity	Operational considerations; formation fluid and rock composite and microbial activity; for new developments: gas tightness
Current locations (operator, start date)	UK: Teesside (Sabic Petrochemicals, 1972) USA: Clemens dome (Conoco Philips, 1983) Spindletop (air Liquide, 2016) Moss Bluff (Praxair, 2007)	None for hydrogen; established use with natural gas and air	None for hydrogen; established use with town gas and natural gas	None for hydrogen; established use with natural gas

Finally, despite the many research advancements in the field of underground H$_2$ storage, it is evident from the presented discussions that many influencing factors on the viability of UHS are still unresolved. In fact, a review by Tarkowski[5] argued that this technology is unlikely to be a feasible one to be practically adopted in the near future. Geological, technological, legal, economic and social factors were cited as the obstacles to its full-scale implementation. Furthermore, it was pointed out that the future potential for lowering hydrogen's production cost *via* electrolysis will be a significant influencing factor on the applicability of UHS on an industrial scale. However, the success of salt cavern UHS in the USA and UK would suggest

long-term viability. Notwithstanding, in light of these points, we present the feasibility of natural H_2, as a complementary alternative with a strong potential to ameliorate the effects of increasing energy demand in Section 3.

3. Natural occurrence of hydrogen

In this study, natural hydrogen refers to the occurrence of H_2 within the earth, independent of human activity. In contrast, we use the acronym UHS to illustrate deliberate efforts made by mankind to store H_2 in underground/subsurface formations.

3.1 Mechanisms

Hydrogen may be formed by the contact of water with rock surfaces containing radicals and radioactive elements like uranium and thorium (water–rock interactions, *e.g.*, cataclasis, radiolysis). Furthermore, the decay of dissolved or solid organic matter by thermal maturation is another formation mechanism; however, this requires significant burial depth to initiate the processes. The relatively low thicknesses of some sedimentary basins over which H_2 has been discovered make this mechanism unlikely.[35] Many bacteria (*e.g. Escherichia coli* and *Clostridium pasteurianum*) are also capable of generating energy

via H_2 oxidation.[89,90] Nevertheless, H_2 produced in this way can also be rapidly consumed by soil enzymes and methanogenic bacteria,[91] thus yielding low overall concentrations. Desorption from subsurface rocks is also a possible mechanism governing H_2 generation (particularly in seepages).[34] It is worth mentioning that these processes may occur in ophiolites, organic-rich sediments, fault zones, igneous rocks, crystalline basements, salt bearing strata, and hydrocarbon-bearing basins.[92,93] The many occurrences of this resource worldwide are a strong indication of a deep-seated origin. The geological location and suggested formation mechanism of the global natural underground hydrogen occurrence with a minimum 40% concentration is presented in Table 4. Additionally, Table 5 summarizes some of the hypotheses proposed in recent contributions.

One of the earliest studies documenting the origin of natural underground hydrogen in the US demonstrated the abiogenic origin of H_2 in 10 Kansas wells near the Mid-continent rift system.[98,99] The average amounts of H_2 ranged from 29–37 mole% H_2, with the rest being mainly N_2. The low concentrations of CO_2 and CH_4 (products of biogenic activity) led to the conclusion that Fe^{2+} oxidation (during serpentinization of ultramafites) is a more feasible explanation for molecular

Table 4 Some discoveries of natural H_2 with more than 40% concentration

Reference	Measured H_2 (%)	Place & country	Geological location & formation mechanisms
Smith *et al.*,[93] Lollar *et al.*[94]	57.8	Sudbury, Canada	Water bodies (radiolysis and hydration reactions)
Morrill *et al.*[95]	50.9	Camp Spring, USA	Ophiolites (serpentinization of cedar *via* shallow and deep water sources)
Vacqand[96]	97	Bahla, Oman	Ophiolites (gas seeps from the surface – serpentinization)
Etiope *et al.*[97]	48.3	Vaiceva Voda, Bosnia and Herzegovina	Ophiolites (serpentinization in water-free or unsaturated rocks hosting metal catalyst)
Coveney *et al.*[98]	96.3	Hoffman, USA	Rift zone (abiogenic origin with reactions involving Fe^{2+})
Zgonnik[29]	80.4	Iriklinskoe, Russian Federation	Igneous rocks (−)
Angino *et al.*[99]	80.5	Nizhny Tagil, Russian Federation	Igneous rocks (−)
Sakai *et al.*[100]	57.3	Namafjall, Iceland	Rift zone (reaction between reduced carbon and water in the magma)
Huntingdon and Sato[101]	57.8	Etna, Italy	Volcanic gases (fumaroles)
Ward[102]	68.6	Penneshaw, Australia	Precambrian rocks (−)
Symonds *et al.*[103]	51.5	Augustine, USA	Volcanic gases (shallow crustal sedimentary rock)
Guelard *et al.*[31]	91.8	Kansas, USA	Precambrian rocks (deep-seated H_2: Water reduction associated with Fe oxidation; reactions occurring in the tubing attributed to high content of reduced iron)
Prinzhofer *et al.*[30]	98	Bourakebougou, Mali	Sedimentary rocks (abiotic origins, associated with neo-Proterozoic sediments)
Nakamura and Maéda[104]	51.4	Arima, Japan	Geysers and hot springs (−)
McElduff[105]	100	Cyprus	Orebodies (chromites as podiform bodies in the mantle)
Dubessy *et al.*[106]	100	Oklo, Gabon	Orebodies (−)
Angino *et al.*[99]	61.5	Muhlhausen, Germany	Salt deposits (mixed origins)
Wood[107]	75.8	Poison Bay, New Zealand	Sedimentary rocks (serpentinization reactions)
Молчанов[108]	81	Pechora, Russian Federation	Coal basins (−)
Молчанов[108] and Zgonnik[29]	>50	Wittelwheim, France	Salt deposits (−)

Table 5 Hypotheses for natural H_2 origin

| Reference	Hypothesis
Larin et al.[109]	Primordial origin, with subsequent global degassing of H_2 from deep down the earth into several sedimentary structures
Shcherbakov and Kozlova;[110] Toulhoat et al.[111]	Originally H_2-enriched earth's interior
Sugisaki et al.[112]	Degassing of the earth's mantle
Isaev et al.[113]	Significant H_2 concentrations in the earth's core
Freund et al.;[114] Larin et al.[33]	Bacterial activity within deep aquifers in sedimentary formations, in the presence of organic matter substrates
Smith[115] Charlou et al.[116]	Water hydrolysis (including water radiolysis, electrolysis, cataclasis, and ferrous metal oxidation)
Zgonnik et al.[35]	Decay of organic matter via thermal maturation
	Decomposition of methane and ammonia at temperatures above 600 °C during metamorphism
Takai et al.[117]	Serpentinization (a process by which ultrabasic rocks are oxidized by water into serpentine, with H_2 produced) – water contact with reducing agents in the earth's mantle

hydrogen's occurrence. Redox reactions of mafic minerals in Precambrian rocks were also suggested as a likely mechanism. However, direct outgassing from the earth's mantle was deemed a less likely mechanism because of the extremely high temperatures therein (unsuitable for H_2 formation via serpentinization). This observation was also confirmed in the work of Zgonnik et al.[35] Larin et al.[33] reported the existence of sub-circular structures (morphological depressions) harbouring hydrogen in the Russian part of the European craton (the Borisoglebsk–Novokhopersk area, Fig. 4f). In one of these structures, they estimated the daily hydrogen seepage at the surface of these structures to be between 21 000 and 27 000 m³. The highest H_2 concentrations in these structures were obtained inside and along the border of the depressions; adjacent regions outside the structure's boundary did not yield a detectable amount of H_2 gas. The observed depressions have been interpreted as the consequence of rock alteration along the migration pathways of subsurface H_2. These are also prevalent in Azerbaijan and Latvia as shown in Fig. 4c and e, respectively.

The presence of H_2 (98% purity) was confirmed in the Bourabougou field of Mali (Fig. 4d) after analyzing data from 12 exploratory wells in the region (8 km diameter).[30] The produced H_2 was utilized for electricity supply (via an internal combustion engine) to the nearby local village. This represents one of the 1st deployments of natural H_2 for energy production. It was further concluded that the exploitation of 1 kg of natural H_2 is within 2–10 times lower than that of manufactured H_2. Significant concentrations of H_2 have been detected in morphological depressions in North Carolina, USA (Carolina bays).[35] The measurements from this study suggested that observed H_2 concentrations are reflective of the complex fluid flow pathways for H_2 gas from deep down the earth to the surface. The study was facilitated by a review of satellite images (in Fig. 4b) showing a high density of bays with varying dimensions and accessibilities. An estimation of the daily H_2 flow from the considered bays was as high as 2700 m³ (Fig. 4b). The authors suggest a possible origin of the observed H_2 – geochemical processes occurring under the sedimentary pile followed by migration of the produced gas to the surface. This pathway for gas migration causes gas–rock interactions that result in the formation of shallow pathways; this is similar to the conclusions derived from Larin et al.[33]

Bay-like H_2 emitting features have been documented to sometimes occur along structural faults.[33,119] These faults tend to act as fluid conduits (preferential migration pathways, due to their high permeability relative to the surrounding rock); they have been suggested as facilitators of H_2 gas seepages observed in morphological depressions. The investigation of continuous H_2 seepage in a circular depression in Brazil (Sao Francisco Basin, Fig. 4a) was studied as a function of space and time.[34] The H_2 emission profile obtained in this study follows temperature and irradiation curves. This indicated that H_2 emission is likely correlated with an evaporation mechanism during soil evaporation. A daily recharge of H_2 in soils was observed, indicating a source of H_2 below the observable surface seepage. A similar observation was made in the San Andreas Fault area.[35,36] Their results also demonstrate that the soil structure cannot only be considered a H_2 sink, as shown in the work of Khdhiri et al.,[120] but also a H_2 emitter. Hundreds of soil gas measurements in Kansas, USA, also suggest that natural fractures are possible preferential channels for the vertical migration of H_2.[121]

Arrouvel and Prinzhofer[122] presented the main reactions responsible for the formation of H_2 via metamorphic processes. The authors conclude that pyritization and serpentinization are complementary reactions, which enhance H_2 formation through an iron cycle. Pyritization refers to the replacement of a material by iron pyrites whereas, serpentinization is a process by which ultrabasic rocks are oxidized by water into serpentine, with H_2 produced. Arrouvel and Prinzhofer[122] also outlined the influence of this process for H_2 production according to the equation shown below.

$$Fe_2O_3(hematite) + 4H_2S(g) \rightarrow 2FeS_2(pyrite) + 3H_2O + H_2$$
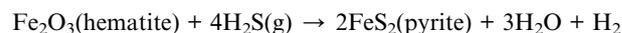
The mechanism of H_2 generation is more likely a complex combination of several redox reactions, which involve water, sulphur and iron. Through simple thermodynamic calculations
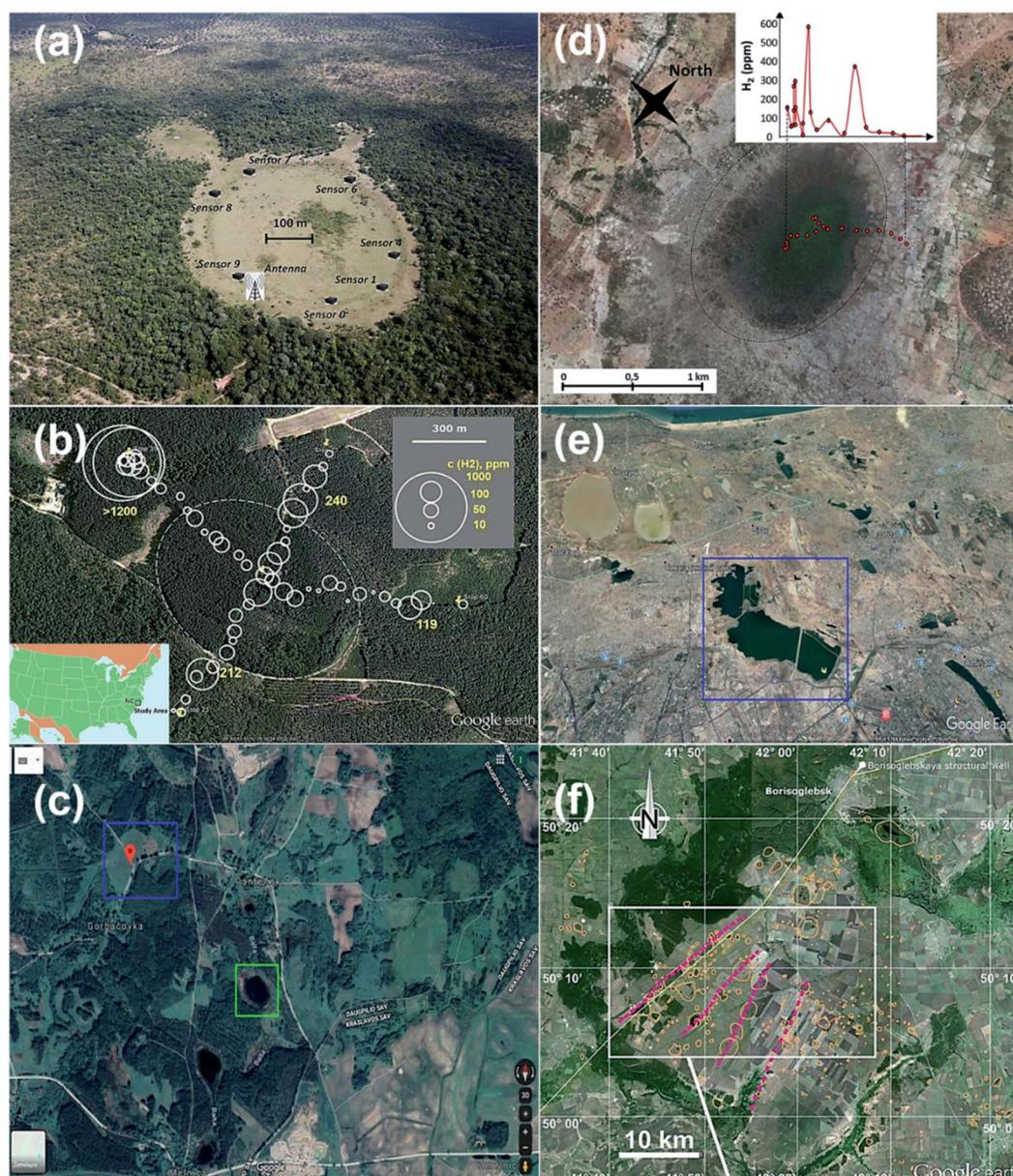
Fig. 4 (a) Sensor positions for H_2 concentration measurements in the circular depression of the San Francisco Basin (Brazil);[34] (b) H_2 concentration measurements in the Smith Bay area of North Carolina (USA), with solid circles illustrating the H_2 concentration in ppm;[35] (c) drilling for H_2 in Latvia (with blue rectangle showing the drilling well location and the green rectangle showing a H_2 degassing region);[118] (d) circular depressions emitting high purity H_2 in Mali, showing the concentration profile;[30] (e) satellite images of local H_2 sites in Azerbaijan formed above basaltic;[118] (f) size distribution of H_2 seepage depressions (rounded orange lines) in the Borisoglebsk–Novokhopersk area of the East European craton in Russia.[33]

(evaluating Gibbs free energy as a function of depth), the authors provided evidence on the geochemical cycles of iron responsible for H_2 production. Considerable H_2 concentrations have also been observed in groundwater obtained from fractured rock samples in drilled wells located in South Africa. The highest concentrations were found in deeper and highly saline fractured aquifers.[123]

The commonly adopted hypotheses for H_2 generation are that of water reduction through iron oxidation and the radiolysis of crustal rocks.[122,124,125] Nonetheless, a combination of the

highlighted processes in Table 3 may be responsible in some locations, and more research is required to prove and further quantify the respective contributions of the highlighted hypotheses. In all hypotheses, however, the formation and liberation of H_2 are thought to be a continuous process. As pointed out by Prinzhofer et al.,[34] the observed recharge was hardly buffered by the presence of water or bacterial activity. Furthermore, in continental Mali, the production of H_2 has been active for 4 years, with wellhead pressures still suggesting continuous migration to the reservoir. Additionally, as
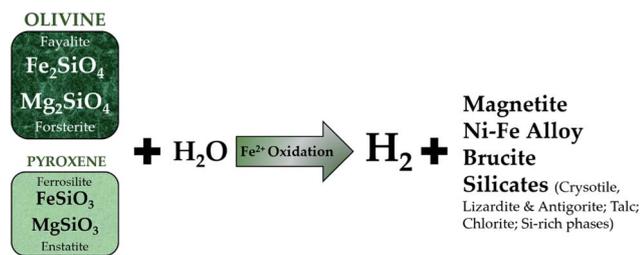
Fig. 5 Serpentinization reaction of olivine and pyroxene for the production of H_2, and various silicates, Ni–Fe alloys and oxides (adapted from ref. 126).

previously shown in Table 4, ophiolites have received significant research attention because H_2 from these locations has often been linked to the well-researched serpentinization process given in Fig. 5.

3.2 Important considerations

The comprehensive review by Zgonnik *et al.*[29] demonstrated that H_2 exists in many more locations than currently identified. Commercial exploitation of this carbon-free resource would require the adaption of some lessons learned from the exploration and production of conventional hydrocarbon resources. We provide some key attributes of natural H_2 systems, which are worth considering, as far as their exploitation is concerned.

• H_2 seepage from circular/elliptical depressions is a likely preliminary indicator for larger H_2 deposits and thus further H_2 exploration within these areas are imperative.

• The high porosity and permeability of most sedimentary or metamorphic rocks and the correspondingly high diffusivity of H_2 may result in small H_2 accumulations in these formations. However, carbonate rocks can absorb (up to 57 times more H_2 than their original content) and retain it for days.[29,127] Hence, these are also potential locations to look out for. Compared to a typical well-defined hydrocarbon system (composed of source rock, permeable carrier rock, and a structural trap/seal), this high H_2 diffusivity makes defining a natural H_2 system challenging.

• The highly diffusive nature of H_2 also implies that it is unlikely to be retained in subsurface traps for extended periods; its reactive combination with O_2 to give water facilitates its complete disappearance.[64] Novel enhanced recovery methods might be required to localize its accumulation in a prospective region.

• The largest accumulations are thought to be found in the Precambrian basement,[33,128] which is hardly the choicest location during hydrocarbon exploration and drilling campaigns. Furthermore, the gas's colourless, odourless, and non-toxic properties are possible explanations for its exploratory obscurity in previous drilling programs. Successful exploration campaigns would involve looking beyond sedimentary basins.

• Measured H_2 concentrations in gas reservoirs have been observed to be 25 times less than H_2 concentrations outside the reservoir's boundaries.[129] It has also been reported that H_2 concentrations are inversely related to hydrocarbon

concentrations in an oil field.[29] These occurrences may be an indication of H_2 reaction with carbon-based fluids or materials. Thus, future H_2 exploration may involve re-evaluating previously abandoned hydrocarbon wells or drilling new wells within their vicinity.

• The large spatial variation in natural hydrogen concentration may be problematic for exploration activities; however, advancements in deviated well drilling technology (*via* sidetracks as usually done in hydrocarbon drilling) will be particularly useful. Periodical changes (abrupt increases and falls[34,112]) would require continuous monitoring. Robust control schemes as already implemented in managed pressure drilling activities in the oil & gas industry will be very beneficial for safe drilling operations, as far as natural H_2 is concerned.[130]

• H_2 exploration & production will significantly depend on the accurate description of potential sealing horizons and high-permeability H_2-conducting fracture zones. As such, the application of robust completion techniques will be vital.[121]

• It has been demonstrated that the upward migration of H_2 through porous media saturated with water is a factor of 10 lower than hydrogen's flux through water. Thus, H_2 migration could be retarded by aquifers.[96] Therefore, water-saturated subsurface formations (if found in regions suspected to have H_2) may act as good H_2 traps.

• Since subsurface H_2 is likely to be consumed by microorganisms, an accurate estimation of the H_2 migration rate can be obtained only if the analysis is conducted below any zone/regions of biological activity.[91] Thus, they should be accounted for during field development projects targeted at H_2 discovery.

4. Complementary overview of underground hydrogen storage and natural hydrogen

Despite the prominent differences in the overall concept/philosophy of UHS and natural H_2, there are considerable similarities in terms of their exploration, utilization and analytical methods (Fig. 6). For example, the significant presence of methanogens[44,131] and homoactogens, which consume free H_2 as an energy source, is essential in identifying potential storage formations and sites, which naturally harbor H_2. On the other hand, the production techniques utilized for artificially stored H_2 will probably be the same as natural H_2. However, these will be affected by site-specific parameters, such as the reservoir pressure, permeability and porosity, which in turn determine the number type, geometry and length of wells. In addition, the difficult-to-store nature of H_2 (ref. 56) implies that techniques which convert the gas to ammonia or formic acid would be beneficial to natural H_2 and UHS projects. These chemicals can be easily transported in their liquid form and can be readily converted back to H_2. Furthermore, identifying a proper sealing mechanism/subsurface rock capable of trapping the gas is crucial for both naturally occurring and artificially stored H_2. Analytical methods capable of characterizing these effects are also likely to be the same (geological and

Scenario	Origin & Mechanisms	Geological Locations	Exploration Considerations	Utilisation & Consumption	Analytical Methods
UHS	Electrolysis, water splitting, gasification.	Salt caverns, depleted reservoirs, depleted aquifers.	Formation tightness, absence of H_2 consuming agents.	Double pathway (into and out of the formation) → increased operational cost. Indirect conversion to ammonia would be beneficial.	Geological models for porous media flow analysis, thermodynamics & kinetics of H_2 gas adsorption on different minerals.
Natural H_2	Formation by serpentinization reactions, water hydrolysis, primordial origin.	Naturally exists in Precambrian basins, ophiolites sedimentary rocks, aquifers, shallow bays.	Natural seepage sites, absence of H_2-consuming bacteria.	Single pathway (out of the formation) → reduced operation cost. Indirect conversion to ammonia would be beneficial.	Field H_2 gas analysers, geological models for analysing flow in porous media.

Fig. 6 A comparison of UHS and natural H_2 attributes and exploitation considerations.

engineering analyses of flow in porous media, as far as appraisal efforts and simulations of gas recovery are concerned).

It is also worth emphasizing the similarities in the types of geological formations considered for artificial UHS and those in which significant natural H_2 deposits have been realized, as evident in Fig. 7. Of all four candidates of artificial UHS concepts, salt caverns are ahead in terms of research and development, with four proven sites for pure hydrogen gas storage in the UK (Teesside) and the USA (Clemens Dome, Spindletop, Moss Bluff) demonstrating long-term storage (40–50 years) potentials. Perhaps, the gas–rock interaction in other subsurface formations where H_2 is naturally occurring can provide further insights into prospective UHS geological locations. Furthermore, the fast diffusivity of H_2 is an issue for subsurface geological storage and affects the extraction from natural or artificial sources through steel alloy pipes; also, the tightness level between connected drill pipes, applicable to conventional oil and natural gas production, may not be directly adaptable to H_2 extraction systems.[19–21,29,82,86,87]

Besides the technical considerations and challenges governing natural H_2 and artificial UHS, the legal, social, environmental and economic aspects cannot be overlooked. As far as the legal requirements are concerned, land development activities of the storage site are expected to conform to national policies. In the UK, for example, it is likely that an open hearing/consultation is held for the public to view the development plan and express their concerns.[132] Lessons can be drawn from the opposition posed by action groups in Yorkshire (UK), regarding the development of a natural gas storage cavern, following leakages observed in some underground storage areas.[133] The potential for these leakages constitutes a significant environmental concern. It may also be argued that the exploitation of underground reservoirs may change the hydrological cycle from its natural condition.[134] This in turn, may trigger adverse

environmental effects, including nitrate accumulation in stored water.

A general overview of the economics of artificial UHS suggests that the required costs may be attributed to exploration (the cost of searching for viable storage sites), storage (the costs associated with transporting the gas to the desired subsurface formation and sealing it there), production/utilization (the costs incurred when the gas is extracted from the formation to the surface for energy generation), and transportation (the costs required to distribute the gas to locations, where it is needed). Conversely, only the exploration, production/utilization and transportation costs are applicable to natural H_2 systems since no cost involvements are directly required for storage (if it is naturally occurring). Thus, when simultaneously considering long-term natural H_2 and UHS projects, it is immediately apparent that additional operational costs will be incurred, with artificial UHS as a result of the double travel path (surface → subsurface & subsurface → surface) by the gas relative to natural H_2 (which would only require H_2 extraction – subsurface → surface). However, direct comparative analyses of these cost components for both systems are scarce in the literature. Also, the explorative costs for suitable storage sites have not been adequately quantified or reported in published literature. The explorative costs for UHS and natural H_2 may be significantly different, despite the similarity in the factors (e.g. presence of seepages, permeability, porosity) considered during the search for viable sites. A more extensive seismic data collection and interpretation is likely to be the case for natural H_2 exploration compared to UHS. The depth and configuration (vertical or deviated) of the wells required is also expected to contribute to this difference in explorative cost of both endeavors. Furthermore, a key difference between the production/extraction phases of UHS and natural H_2 lies in the number of wells that will be required. It is expected that that the wells drilled during UHS will be readily
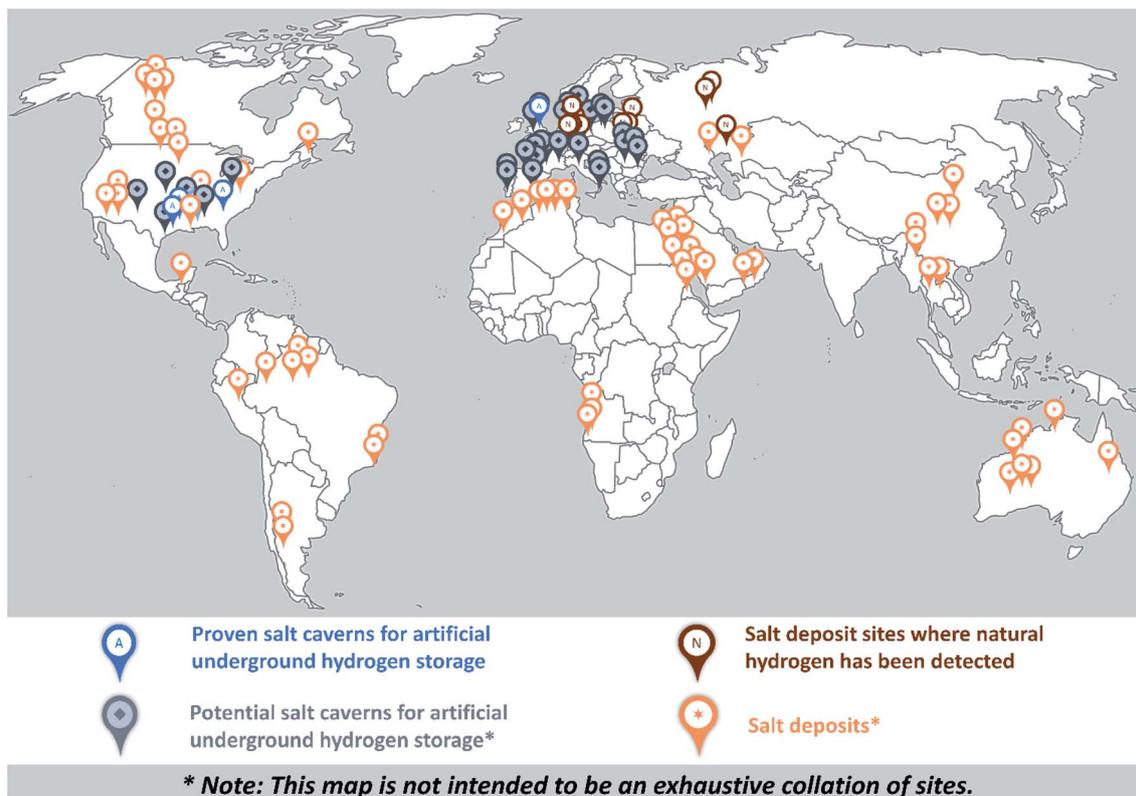
Fig. 7 Overview of proven salt caverns for UHS (USA: Moss Bluff, Clemens Dome, Spindletop, & UK: Teesside) denoted "A"; some potential salt caverns, denoted "◆"; salt deposits where natural H_2 has been detected as free gases (>10% concentration); and some salt deposits across various countries. Figure produced based on the data obtained from the following ref. 19–21, 29, 51, 82, 86 and 87.

applicable for its extraction. Although more extraction wells may be required with UHS, the exploratory wells drilled to prove the viability of a natural H_2 deposit, will be insufficient for the full development of the discovered field. This difference is likely to make drilling cost of natural H_2 exploitation twice as expensive as conventional UHS drilling or even greater, depending on the size of the hydrogen field. As far as H_2 gas transportation is concerned, it has been reported that a 40 000 kg truck is required to transport only 300 kg of H_2 gas – a very low transport efficiency.[135] This paves the way for H_2 liquefaction, which is very costly. The use of H_2 pipelines appears unlikely until it has gained significant penetration into the energy mix as determined by the distribution economics.

As with natural gas, the exploitation of natural H_2, can be considered to consist of the exploration phase (searching for natural H_2 deposits); the appraisal phase (investigating the volume of natural H_2 reserves); the development phase (installing drilling & processing equipment); the production phase (extraction of natural H_2 from identified deposits) and the abandonment phase (uninstalling facilities when the field is deemed non-viable). Despite the differences between natural gas and natural H_2 exploitation considerations, and the absence of economic data on natural H_2 exploitation, the economics of both endeavours have considerable similarities in several aspects; thus, we briefly present information on the economics

of shale gas development in the UK and try to draw insights which may be beneficial to natural H_2.

According the methodology proposed by Ahmed and Rezaei-Gomari[136] for subsurface shale gas extraction in the UK, an analysis of the economic feasibility of natural H_2 production, may begin by establishing 3 candidate development plans, after which a probabilistic financial model can be utilised to generate a distribution of potential gas prices. Based on their study, the average gas well drilling cost, (a significant component of the capital expenditure), in the UK (Bowland shale development) has been estimated to be $17 MM. However, it is important to mention that this cost includes fracking related technical costs (up to 20% of the original well development and completion costs), which may not be incurred, when drilling for natural H_2 (depending on the properties of the formation containing natural H_2). Another component of the capital expenditure – the land acquisition costs, has been given a range of $6 M–$16 M acre^{-1} for Bowland shale development in the work of Acquah-Andoh.[137]

Similarly, in the work of Ahmed and Rezaei-Gomari,[136] a fixed annual operating expenditure (OPEX) of $25 000 was applied, together with a 15% overhead. Whereas, the variable operating expenditure, was assigned a mean value of $1.5 per Mcf. These values were derived from the comprehensive report of shale gas exploitation in the UK, where a variable OPEX was obtained as £0.5 MM per Bcf, or approximately $0.7 per Mcf in

addition to 2.5% of the CAPEX each year[138] Again, as with the CAPEX, these values for the OPEX, account for fracking costs, which may not be incurred during natural H_2 production.

In addition to the above costs, gas processing costs may be incurred to raise the purity of produced natural H_2 to the desired levels. Most natural H_2 discoveries have been accompanied with gases such as CH_4, CO_2, N_2 and He. Membrane separation,[139] pressure swing adsorption and cryogenic distillation technologies may be employed to achieve efficient separation. However, it is worth pointing out that the necessity of such separation and the degree to which it is applied depends on the geological location of the discovered H_2 resource. For example, the discovery in Mali (98% H_2 concentration) may be directly utilised for energy generation *via* internal combustion without this extra processing step. As far as the exploitation of natural H_2 is concerned, currently identified seepages worldwide, may constitute locations for initial exploration, as conventionally done with oil and gas exploration. Nonetheless a deliberate exploration attempt has to made, if this resource is to be tapped, particularly because a majority of the currently highlighted discoveries were accidental. In some countries, H_2 is not classified as a minable resource; thus, a reclassification of natural H_2, is necessary in order to obtain exploration and production permits in different geographical locations. Besides the search for large natural H_2 deposits, the degassing of water from wells drilled into fractured serpentines,[140] may also prove a viable H_2 source, to be further investigated, during which hydraulic fracturing technologies may be applicable.

In the absence of a detailed economic analysis of natural H_2 exploration, extraction and transportation in literature (a subject beyond the scope of this review), we present a brief discussion on the economics of artificial UHS in Section 4.1. It is also important to highlight that the production/utilization-related costs are not captured – also beyond the scope of this review, but worthy of consideration in future research endeavors.

4.1. Economic analysis of artificial UHS

Underground hydrogen storage cost is dependent on the transportation, monitoring, storage, and injection cost.[5] The cost of storage is also dependent on the location and properties of the geological storage site. A potential leak point in the storage site could increase the cost of storage, especially for porous rocks. In a scenario involving salt caverns, tightness tests are performed before each cavern is licensed, confirming whether the cavern is suitable for hydrogen storage. Earlier conceptual studies showed that large-scale hydrogen storage in underground deposits is inexpensive compared to other storage technologies.[4] Moreover, the main identified capital costs incurred during UHS include the costs of gas compression, transformer installation, piping, transformer installation, new well drilling and wellhead equipment installation. Tarkowski *et al.*[13] stated that the cost of constructing and operating hydrogen storage in aquifers is greater than that in depleted hydrocarbon reservoirs and caverns.[5] Moreover, depleted natural gas reservoirs have a lower construction cost when compared with depleted oil reservoirs. In terms of

storage cost, the cavern system has the lowest cost among the three media.[5]

Abandoned reservoirs are the cheapest among all possible storage systems, followed by the solution and hard rock caverns.[5] Techno-economic analysis of several caverns with different depths and volumes showed that the overall cost of the projects is identical. Although, each cost component differs. For instance, deep storage sites are associated with high surface installation primarily for gas compression. On the contrary, shallow sites have a lower surface installation cost as well as a very high cavern construction cost.[141,142] In another study, the capital expenditures of hydrogen storage in different geological sites are assessed and presented in Fig. 8.[143] It should be noted that the data and economic model used to estimate the capital cost are peculiar to the publication year 2014.

Based on the cost analysis (Fig. 8a), the depleted oil and gas reservoirs are the most economically viable storage medium with a levelized cost of 1.29 \$ kg^{-1}. The hard rock caverns system is the most expensive, with a levelized cost of 2.77 \$ kg^{-1}. In a more recent study, the techno-economic feasibility of large scale UHS in France was evaluated.[145] The overall cost of hydrogen including storage cost ranges from €4.5 kg^{-1} to €6.6 kg^{-1} H_2. The authors noted that the cost of UHS in salt caverns constitute about 5% of the total hydrogen cost.

Michalski *et al.*[146] assessed the business potential of underground hydrogen storage in salt caverns in Germany. Macro- and microeconomic analysis was used to determine the dimensions and optimal location of promising hydrogen storage sites. They noted that the integration of UHS technology with electrolytic hydrogen production could foster power production and distribution systems in Germany.[146] Recently, Singh[144] performed a comparative techno-economic analysis of hydrogen storage in inactive horizontal shale gas wells and underground storage facilities (Fig. 8b–e). The analysis was performed by using a numerical model representing an hydraulically fractured depleted shale gas with the properties of Haynesville shale and its horizontal wells. Singh results shows that the capital expenditure of storing hydrogen in depleted shale wells (\$0.73 kg^{-1}) is lower than salt cavern (\$1.51 kg^{-1}). Additionally, the operating expenses is also lower (\$0.11 kg^{-1}) when compared to salt cavern (\$0.14 kg^{-1}). The author stated that the capital expenditure of hydrogen storage in shale lateral wells is dependent on the existing surface facilities such as the gas compressor station at the well – pad.[144]

Wu *et al.*[147] presented a techno – economic assessment framework for hydrogen storage by considering four different case studies including the storage of hydrogen in an underground salt cavern for longer periods and fuel cell for regeneration. The other scenarios considered by the authors includes the direct injection of hydrogen into gas networks and the bulk sale as transportation fuel and industrial gas. Their result shows that the UHS in salt cavern is a promising technology with a present value of \$47 million and benefit cost ratio of 1.28. In contrast, hydrogen injection into the gas network has a present value of \$18.3 million and benefit cost ratio around one. However, detailed techno-economic and life cycle assessments are still

required to compare the economic and environmental feasibility of various underground hydrogen storage sites.

5. Recommendations for future research

Based on the critical assessment of UHS and natural H_2 systems presented, the following points constitute future research areas, which are worth investigating:

• Geomechanical studies should be conducted to assess the widely reported high-cycling capabilities of rock salt, taking into account its rheological properties. These analyses, combined with thermodynamic conditions, should form the basis for simulations to predict accurate injection and withdrawal timings and ultimately exploit the high cycling potential.

• The potential of H_2 escape and unwanted migration outside the subsurface boundary should be a key decision factor, as far as the acceptance or rejection of a candidate
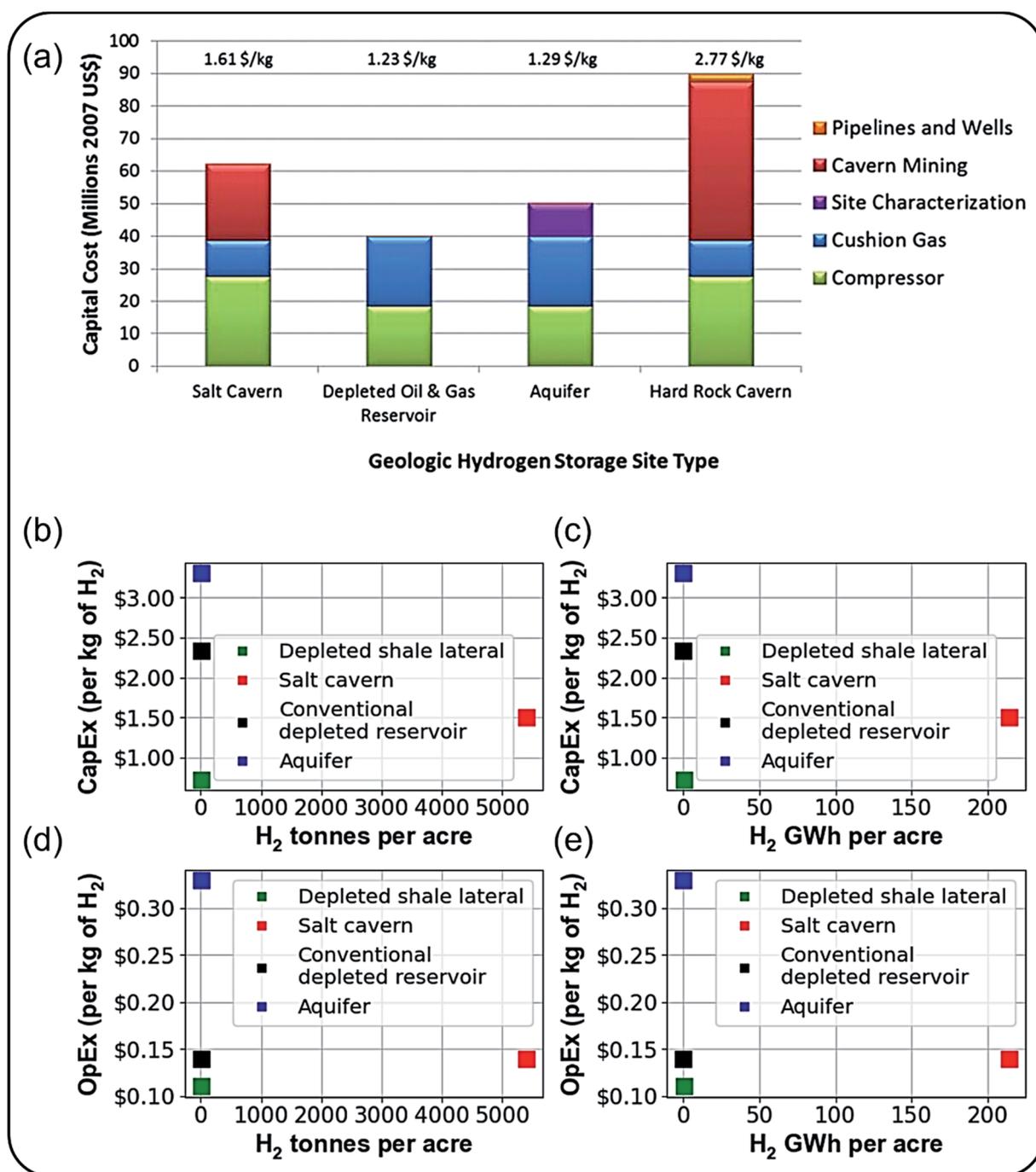

Fig. 8 (a) Comparative capital expenditures of hydrogen storage in different geological sites;[143] (b–e) hydrogen storage costs versus storage density per acre for different storage systems.[144]

location is concerned. Thus, the accurate determination of site-specific timeframes over which H_2 can be artificially stored (with minimal loss) is vital for the assessment of prospective underground locations. Furthermore, the cyclability of these sites is a crucial factor to be determined for long-term usage.

• To improve the reliability and durability of rock caverns, an intensive campaign of compatibility experiments must be conducted to build a database of materials, taking into account site variability and uncertainties associated with UHS.

• The areas of subsurface hydrogen (both natural and artificial) may well benefit from twinned explorations, mainly to build an understanding of the similarities and differences between factors like microbial interactions and formation stability. Lessons learnt can be mutually beneficial to communities within both areas and could progress research and development considerably.

• The sealing effect of natural H_2 in the subsurface rock systems is still not well understood in relation to other gases present. Robust chemical modelling of gas–water interactions which govern gas migration is necessary. Advection and diffusion parameters as well as relative permeability and water solubility data, would be required for model development.

• Standard analytical methods for gas chromatography often utilize H_2 as the carrier gas; this causes problems for large-scale detection of H_2. Thus, there may be several occasions where this valuable resource has not been identified in H_2-rich samples because of the lack of robust detection techniques for accurate measurements.

• Considering the uncertainty surrounding natural H_2 exploration and production, further research is required on the techno-economic assessment of natural H_2 exploratory projects. In addition, a comprehensive economic and lifecycle analysis of different types of UHS systems should be assessed. However, full-scale field development studies will be required to first, quantify the volume of natural H_2, within an identified formation, before extensive economic analyses.

• Natural hydrogen exploration and production, will also benefit from conventional production optimisation methodologies applicable to oil and gas fields. Thus, similar studies to those reported in ref. 148 and 149 will be worth pursuing.

• Recently Proton Energies Ltd has devised a method of cheaply producing H_2 from underground oil, gas and coal-bed fires. The procedure involves igniting subsurface hydrocarbon deposits by pumping air or oxygen. At temperatures above 500 °C, injected steam reacts with hydrocarbons to produce syngas, CO_2, and more H_2. The application of a novel Pd-alloy catalyst induces a selective diffusion of hydrogen to the surface, whereas other gases remain underground. While real-world testing of this technology is ongoing, there is a great potential of this technology to facilitate low-cost production of clean H_2 if successful.

6. Conclusions

This review discussed the natural hydrogen production mechanisms and, most importantly, hydrogen storage technologies in detail. Underground hydrogen storage is suggested as a safe method considering the limited hydrogen contact with atmospheric oxygen. It is also effective in long-term ($\sim$40–50 years) high energy storage density (up to 250 W h L^{-1}). UHS in salt caverns was identified to be the most researched technology with four established sites in the USA (Clemens Dome, Spindletop, Moss Bluff) and the UK (Teesside). Leakage issues constitute a significant problem with UHS especially in porous rocks due to its molecular size, low density, and viscosity. According to the capital cost analysis, the depleted oil and gas reservoirs are determined to be the cheapest storage option with a cost approximation of 1.29 \$ kg^{-1}. In comparison, the hard rock caverns system is identified as the most expensive, with a Levelized cost reaching 2.77 \$ kg^{-1}. Additionally, the capital expenditure of storing hydrogen in depleted shale wells (\$0.73 kg^{-1}) is lower than salt cavern (\$1.51 kg^{-1}). With regard to natural H_2, the successful deployment of this resource for energy production in Mali is proof that this technology has the potential to compete favourably with fossil fuel energy sources. Despite the scarcity of economic data on natural H_2 projects, it is expected that the overall economics of its extraction will not be too different from natural gas. Nonetheless, this requires further substantiation *via* robust techno-economic analyses. An improved understanding of natural Hydrogen's formation mechanisms is also likely to facilitate future exploratory campaigns of this readily available resource. The exploitation of natural H_2 will involve the 5 phases of conventional oil and gas exploitation, including: exploration, appraisal, development, production and abandonment phases. Further field-development studies, capturing these phases, will be required to prove its economic viability.

Conflicts of interest

There are no conflicts to declare.

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