Hydrogen-induced mineral alteration: A review in the context of underground hydrogen storage (UHS) in saline aquifers

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ABSTRACT

Hydrogen is considered a viable energy vector, it can be produced through the electrolysis of water and stored as a gaseous phase in the subsurface. Hydrogen storage in saline aquifers is not yet commercially operational, to increase the technological readiness, the complex interactions between rock, pore fluid, and hydrogen under reservoir conditions (increased pressure and temperature) need thorough understanding. It is acknowledged that abiotic geochemical reactions are a potential barrier for UHS as hydrogen is an electron donor and can form highly reactive hydrogen ions. Using a comparative approach, this study reviews the current disparity in the literature regarding the impacts and extents of hydrogen-induced abiotic reactions, to identify knowledge gaps requiring further investigation. Data from both experimental and modelled methods are summarised in relation to individual minerals, common in the subsurface, and their implications to efficiency and security of underground hydrogen storage. This review demonstrates a significant agreement concerning the lack of reaction between hydrogen and rock-forming silicate minerals, and a strong likelihood that under reservoir conditions (heightened temperature and pressure) hydrogen can reduce pyrite to pyrrhotite. It also reveals compelling evidence suggesting exposure to hydrogen can lead to the dissolution of sulphates (anhydrite) and carbonates (calcite). We conclude development of future hydrogen storage projects in saline aquifers should therefore focus on silicate-rich formations. And further work is needed to establish a clear understanding of extents and rates of potential mineral reactions to ensure storage security and efficiency in future projects.

1. Introduction

For UHS to become a reality, uncertainty associated with hydrogen-loss and changes to reservoir integrity should be quantified and reduced through increased understanding and quantification of geochemical reactions (Bo et al., 2021). The focus of this review is abiotic reactions caused by the introduction of hydrogen into porous subsurface reservoirs and a mixture of experimental and modelled results from the literature are discussed. It is important to collate the recent wave of new results surrounding hydrogen-induced geochemical reactions to determine what agreements have already been made, and to identify outstanding knowledge gaps, to inform future studies. This work will address discrepancies in the literature regarding the presence and extents of reactions, providing an evaluation of current knowledge and crucial insights into where further investigation is required.

1.1. Role of hydrogen in energy storage

One viable option for a large-scale energy vector is hydrogen (UK Hydrogen Strategy, 2021). It is a clean energy carrier that can be produced through a variety of ways including carbon-neutral electrolysis of water (known as 'green hydrogen'). Hydrogen has a higher energy density per mass than any hydrocarbon, but its low physical density means a large storage volume is required to match the current energy storage capacity of natural gas (Yetka et al., 2018; Zivar et al., 2020; Tarkowski et al., 2021). The considerable space of the subsurface is the only practical alternative for large-scale hydrogen storage, due to its relatively cheaper costs and anoxic conditions (Zeng et al., 2023a). The storage of gas underground is not a novel idea and is already an established technology in the petrochemical industry (Al-Shafi et al., 2023). However, underground storage of hydrogen is thought to be more complicated than natural gas storage due to its higher reactivity, volatility, and lower density (Yetka et al., 2018; Al-Yaseri et al., 2023a).

Therefore, experience cannot be directly translated to UHS (Zivar et al., 2020; Tarkowski and Uliasz-Misiak, 2022).

1.2. Current storage methods and their limitations

Currently, pure hydrogen is commercially stored in solution-mined salt caverns in the UK and US (such as Teesside, UK, and Gulf, US) (Al-Yaseri et al., 2023b). Salt formations possess numerous favourable geological characteristics for storage, including tightness and self-healing properties, mechanical stability, resistance to chemical reactions, and caprock integrity. Moreover, caverns can be engineered safely, and the harsh saline conditions are believed to limit microbial consumption of hydrogen (Al-Yaseri et al., 2023b). However, suitable deposits are geographically limited, as a result, they may not be ideally suited for the high-frequency storage cycles anticipated in a 'hydrogen economy' (Foh et al., 1979; Al-Yaseri et al., 2023c). The imperative for alternative storage solutions favours porous media storage, where gas is stored within the void spaces of sedimentary rocks including saline aquifers and depleted gas reservoirs (Fig. 1). These formations are both stratigraphically more abundant and geographically widespread, offering significant potential for accommodating the necessary storage capacities (Carden and Paterson, 1979).

Key prerequisites for a storage site include adequate trapping mechanisms to prevent hydrogen migration beyond the reservoir limits and ample capacity to support storage on a TWh (UK Hydrogen Strategy, 2021), as an estimated 150 TWh of seasonal hydrogen storage is required to decarbonise gas in the UK (Scafidi et al., 2021). Optimal storage entails a highly permeable and porous reservoir rock, overlain by an unfractured, impermeable caprock. For efficiency, the reservoir rocks permeability should fall within the range of 2 and 600 mD, to facilitate the required injectivity and withdrawal rates (Zivar et al., 2020; Thiyagarajan et al., 2022). The caprock prevents upwards gas migration, with its sealing efficacy dependent upon low permeability and high capillary pressure. Water-wet caprocks are advantageous due to their high threshold pressure, providing an additional barrier against hydrogen penetration (Zivar et al., 2020).

As commercial storage of pure hydrogen in saline aquifers is yet to be undertaken, and demonstration projects are limited to RAG Underground Sun (EUH2STARS, 2024a, 2024b) and HyChico (Pérez et al., 2016) globally, laboratory experimentation remains essential to provide thorough investigation and evaluation of potential interactions between hydrogen and the subsurface. Experimentation, even when limited to

shorter timescales (months), not years as expected for storage operations, help identify subtle changes and hence evidence of reactions. Critical factors to review include hydrogen-loss and/or trapping through diffusion and reactions, degradation of hydrogen purity from reaction products, and the extent of geochemical activity expected during UHS (Yetka et al., 2018; Bo et al., 2021; Al-Yaseri et al., 2023a). These depend on operating conditions such as temperature, pressure, salinity, pH, rock wettability, and rock-fluid interfacial tension (Al-Yaseri et al., 2023d).

This review will evaluate the effect of hydrogen on different mineral groups based on results published in the literature. The main groups that constitute average reservoir and caprock mineralogy are: carbonates (CO_3^{2-}), clay-minerals, sulphates ($SO4^{2-}$), silicates (SiO^{4-}), iron-oxides, and iron-sulphides; will be discussed in turn, and their likelihood for reaction assessed. Based on these results, the implications for UHS efficiency and security will be considered, and suggestions regarding future experimental design will be made.

2. Underground hydrogen storage in saline aquifers

2.1. Mineralogy of reservoir and caprock

The mineralogy of reservoir and caprock has been characterised in other storage and recovery applications such as Carbon Capture, Utilisation and Storage (CCUS), geothermal energy, enhanced oil recovery, and legacy petroleum exploration. The mineralogy of sedimentary rocks is immensely diverse, reflective of the rocks depositional and diagenetic history, and further influenced by the reservoir's current temperature, pressure, and salinity (Flesch et al., 2018). Macroscopically homogeneous rocks can contain a variety of different minerals once analysed. Mineral assemblages can be split into major minerals that constitute the bulk composition, and minor minerals that are present in lesser or trace amounts. A further differentiation can be made between mineral grains and cement, as although both may contain reactive minerals, the effect of interactions may result in very different impacts. Minerals considered compositionally major likely provide intrinsic properties, such as structure and texture, that if extensively altered could have negative impacts on the mechanical properties of the subsurface. As minor minerals are lesser in abundance, their alteration is less likely to affect bulk reservoir properties. However, products of reactions and secondary reactions triggered by initial alteration may cause further detrimental effects, both on host rock and stored hydrogen. The most inert rocks will therefore constitute the most suitable reservoir and caprock formations.

2.2. Geochemical and mechanical implications of UHS

Storage within porous reservoirs involve injecting hydrogen into the subsurface, disrupting the chemical equilibrium between pore fluid and rock matrix (Heinemann et al., 2021; Navaid et al., 2023). This may lead to alterations in the subsurface environment, including reactivity, which in turn influences petrophysical properties, such as porosity, permeability, pore structure, and mineralogy (Navaid et al., 2023; Zeng et al., 2023b). If apparent these alterations bear significant implications for storage safety, ensuring minimal leakage, and the recoverability of high-purity hydrogen (Perera, 2023). However, it is notable that the solubility of hydrogen in pure water is relatively low, approximately 0.00016 mmol/L at 25 °C and 0.1 MPa (Lv et al., 2024), in contrast to other gases, such as CO_2, which exhibits a much higher solubility of around 1.45 mmol/L under similar conditions (Dodds et al., 1956).

As hydrogen has as high buoyancy, the hydrogen plume is likely to accumulate below the caprock due to gravity segregation, emphasising the need of ensuring the caprocks sealing efficacy (Perera, 2023; Nazari et al., 2024). Interactions within the three-phase system (rock, pore fluid, stored gas) are complex and may impact geochemical and rock-mechanical properties (Zeng et al., 2023a), such as mineral alteration as known from CCUS research (Hemme and van Berk, 2018). Of particular concern in UHS reservoirs are abiotic redox reactions, where
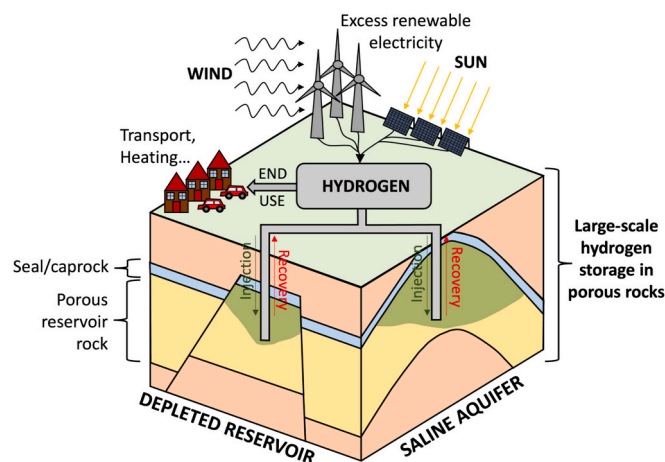

Fig. 1. Overview of the hydrogen economy.
Excess renewable power generation during times of favourable weather conditions can be used in electrolysers for green hydrogen generation. Hydrogen can then be stored in the subsurface until times of need at large-scale (TWh). It can be converted back to electricity, or used in gaseous form in power, heating, and/or transport.

hydrogen, acting as an electron donor, may trigger the reduction of electron acceptors such as sulphates, Fe(III), and Mn(IV) in host rock mineralogies (Truche et al., 2010; Berta et al., 2018; Hassanpouryouzband et al., 2022).

The presence of microbes in the subsurface can induce significant mineralogical and geochemical transformations within the reservoir and caprock (Zivar et al., 2020). Elevated concentrations of hydrogen will allow for surplus nourishment of microbial communities that usually strive for hydrogen (Berta et al., 2018). This is an important relationship as abiotic reactions tend to proceed slowly even when thermodynamically favoured, but microbial processes can act as catalysts to accelerate these reactions. Metabolic by-products, such as hydrogen sulphide gas, produced by sulphur-reducing bacteria (SRB), can lead to acidification of pore fluids and subsequent mineral alteration (Reitenbach et al., 2015). Additionally, the formation of biofilms may impede permeability by clogging pores, however this review does not consider the effects of geomicrobiology.

In existing literature, it is suggested that carbonate and sulphate minerals, such as calcite, dolomite, siderite, gypsum, anhydrite, and baryte, as well as feldspar, and chlorite-group clay minerals may undergo dissolution under UHS conditions (Reitenbach et al., 2015). Mineral dissolution may enhance permeability by creating new pathways for gas migration within the reservoir and caprocks. It can also influence the mechanical properties of the subsurface, as the removal of load-bearing minerals and cements weakens the formation, consequently leading to increased potential for deformation (Heinemann et al., 2021). The cyclic loading associated with subsurface hydrogen injection and withdrawal may exacerbate these conditions but is likely mitigated by using quartz-dominated formations. Furthermore, if cements such as carbonates dissolve, further reactions may occur with minerals previously isolated from the pore fluid and stored gas (Henkel et al., 2014). Oversaturation of pore fluids with alteration products can trigger precipitation of new minerals and salts, impacting permeability through clogging of pore throats and gas migration pathways (Al-Yaseri et al., 2023a; Heinemann et al., 2021). The balance between dissolution and precipitation therefore significantly influences the reservoir efficiency and caprock sealing ability by altering pore volumes and connectivity (Berta et al., 2018; Yetka et al., 2018; Zivar et al., 2020; Perera, 2023). Moreover, precipitation of minerals in hydraulic fractures and/or dissolution of minerals in closed fractures can also greatly alter the intrinsic strength and storage security of the subsurface (Singh, 2022).

Ultimately, any chemical reaction, mineral dissolution, or mineral precipitation can alter the mechanical properties of the subsurface. This emphasises the need for a comprehensive understanding of potential reactions, their extents, rates, and impacts on reservoir properties over the operational lifespan of a subsurface storage facility. This is crucial for demonstrating the security and efficiency of subsurface reservoirs in determining storage potential and securing investment and necessary permits for development (Reitenbach et al., 2015; Yetka et al., 2018; Bo et al., 2021).

3. Hydrogen-brine-rock interactions

3.1. Addressing uncertainties in hydrogen-sandstone interaction studies

Investigation into hydrogen-sandstone interactions traces back to the 1970s when a global energy crisis spurred exploration into alternative energy sources (Carden and Paterson, 1979; Foh et al., 1979). These initial experiments focussed on single-mineral reactions at relatively low temperatures and pressures (<40 °C, <10 MPa), neglecting the influences of pore fluid composition (Flesch et al., 2018). Therefore, incorporating these conditions into experiments and models is imperative as they influence kinetics and geochemical reactions. With the resurgence of interest in alternative energy sources, there has been a revival in experimental studies investigating underground hydrogen storage. For instance, Truche et al. (2010) and subsequent studies (e.g.,

Truche et al. (2013)) have documented the kinetics of pyrite to pyrrhotite reduction by hydrogen. Furthermore, the reactivity of hydrogen in sandstone has been extensively studied by Yetka et al. (2018) and the petrographic/petrophysical changes in reservoir sandstones following hydrogen exposure have been explored by Flesch et al. (2018), Bo et al. (2021), and Hassanpouryouzband et al. (2022). Due to the impracticality of running experiments for extended durations, models have been developed to predict impacts over reservoir timescales, such as those by Hemme and van Berk (2018) and Bo et al. (2021). A summary of cited works is provided in Table 1.

Truche et al. (2013) concluded that abiotic hydrogen reactions are kinetically constrained, suggesting that they should remain insignificant at storage conditions, even over geological timescales, depending on the concentrations of dissolved hydrogen (Berta et al., 2018). Although this did not consider the cycling frequency of storage expected with UHS. In the context of UHS, dissolution of hydrogen may result in concentrations of several millimoles per litre due to the relationships between increasing depth, increasing pressure, and increasing gas solubility following Henry's Law (Berta et al., 2018). The study highlighted the strong effect hydrogen has on framboidal pyrite, resulting in reduction, dissolution, and the precipitation of pyrrhotite, with no reactions observed with other minerals like clay, quartz, and calcite at low temperatures. This finding aligns with the experimental work on clay minerals by Didier et al. (2012), which found minimal reductions in structural Fe(III) in clays at temperatures below 350 °C, while natural clays remained stable under conditions more realistic of underground hydrogen storage (90 °C). Yet, experimental results by Yetka et al. (2018) suggested hydrogen-induced redox reactions with iron-bearing minerals such as hematite, indicating the need for further investigation to validate these findings.

Reitenbach et al. (2015) suggested that hydrogen storage in rocks could induce the dissolution of sulphate minerals, carbonates, chlorite-group clay minerals, and feldspars leading to the precipitation of iron-sulphide bearing minerals (e.g., illite, and pyrrhotite). This is supported by the findings of Flesch et al. (2018), where different extents of carbonates (Ca/Mg/MnCO$_3$) and anhydrite (CaSO$_4$) alteration, as well as complete pore-filling cement dissolution leading to an increase in porosity in some samples, were observed. However, models by Hemme and van Berk (2018) contradicts these findings, showing an overall decrease in porosity due to the precipitation of K-feldspar, kaolinite, and dolomite outweighing the alteration of quartz, calcite, illite, baryte, and anhydrite. Additionally, Al-Yaseri et al. (2023d) concluded that hydrogen interactions with carbonates are minimal and unlikely to be significant at reservoir scales. This contrasts with models by Bo et al. (2021), which suggested hydrogen-saturated aqueous solutions almost does not react with silicate and clay minerals, but carbonates, like calcite, may trigger up to 9.5 % hydrogen loss due to dissolution induced by hydrogen dissociation processes.

Recent extensive studies by Hassanpouryouzband et al. (2022) concluded that there is no risk of hydrogen loss or reservoir degradation in sandstone reservoirs due to abiotic reactions from underground hydrogen storage. However, discrepancies in results outlined above suggests that some level of abiotic reaction does occur, necessitating further investigation in this field. New experimental results will contribute to future models that may reduce uncertainties associated with recently published models as parameters become more refined and better understood.

There is less attention given in the literature to the integrity of caprocks as seals for hydrogen storage reservoirs, even though buoyancy will force hydrogen to migrate upwards and be in direct contact with the caprock. Mudstones are considered effective seals due to their low porosity, permeability, and high capillary pressures that can prevent hydrogen leakage or significantly reduce hydrogen migration rates (Al-Yaseri et al., 2023c). They have been demonstrated to be gas-tight for methane where forming seals to depleted gas fields, although there is less certainty associated with the integrity of saline aquifer targets.

Table 1
Summaries of literature.*

Work	Sample	Experiment					Analytical Methods	Results	References
		Type.	Temp. (°C)	Pres. (MPa)	Duration	Wet/Dry			
Kinetics of pyrite to pyrrhotite reduction by hydrogen in calcite buffered solutions between 90 and 180 °C: Implications for nuclear waste disposal	Simplified calcite-pyrite assemblages	Batch-reactor	90-180 °C	0–1.8 MPa	300 h	NaCl solution	XRD; SEM	Pyrite reduction to pyrrhotite (dissolution-precipitation reaction).	Truche et al. (2010)
Adsorption of hydrogen gas and redox processes in clays	Claystone & synthetic clays	Batch-reactor	90-120 °C	0.01–0.4 MPa	30–40 days	Dry	Hydrogen adsorption on clays; GC; ^{57}Fe Mossbauer Spectrometry	Up to 0.11 wt% of hydrogen is adsorbed on clays, and up to 6 % of total structural Fe (III) initially present in synthetic clays is reduced on adsorption of hydrogen gas.	Didier et al. (2012)
Sulphide mineral reactions in clay-rocks induced by high hydrogen pressure	Claystone	Batch-reactor	90-250 °C	0.6–3 MPa	150 h – 3 months	Water	Solution chemistry; SEM; XRD	Pyrite reduction to pyrrhotite (lower temp and partial pressure rate controlled by pyrite dissolution; higher temp and partial pressure rate controlled by pyrrhotite precipitation). Absence of reaction with anything else.	Truche et al. (2013)
Mineral reactions in the geological underground induced by H_2 and CO_2 injections	670 reservoir sandstone and clay/silt caprock samples.	Batch-reactor	*Specific reservoir conditions not explicitly stated in paper.*			Synthetic formation fluid	Polarised light microscopy; Field-Emission SEM; EDX; EMS; WDX; XRD; ICP-Mass Spectrometer; ICP- Optical Emission Spectroscopy; XRF; μXCT; BET SEM; μXCT	Visual change in synthetic formation fluid from colourless and transparent to brown and presence of < μm sized solids, likely linked to reaction with iron.	Henkel et al. (2014)
Hydrogen underground storage- Petrographic and petrophysical variations in reservoir sandstones from laboratory experiments under simulated reservoir conditions	Sandstone	Batch-reactor	<40 °C	10–20 MPa	~6 weeks	Synthetic formation fluid		Alteration of sulphate and carbonate minerals, as well as complete pore-filling cement dissolution in some samples.	Flesch et al. (2018)
Hydrogeochemical modelling to identify potential risks of underground hydrogen storage in depleted gas fields	Sandstone	Model	40 °C	40 MPa	30 years	Water	PHREEQC	Decrease in porosity due to precipitation of K-feldspar, kaolinite, and dolomite outweighing the alteration of quartz, calcite, illite, baryte, and anhydrite.	Hemme and van Berk (2018)
Evaluation of geochemical reactivity of hydrogen in sandstones: Application to geological storage	Reservoir sandstones	Batch-reactor	100 & 200 °C	10 MPa	1.5–6 months	Dry and with water	Optical microscopy; XRD; SEM; EDX; EMS	Increase in XRD peak intensity of muscovite and FeO_x following exposure to hydrogen. No textural evolution of minerals observed.	Yetka et al. (2018)
	Sandstone minerals	Equilibrium model	100 °C	1–10 MPa	Instantaneous equilibrium?	Water	PHREEQC	Reduction of Fe from Fe3+ in mainly hematite to Fe2+ in magnetite, fayalite, wustite, and ferrosilicate. Quartz and K-feldspar remain stable.	
	Sandstone minerals	Kinetic model	100 °C	1–10 MPa	100 years	Water	PHREEQC	No major effect on abundant minerals like quartz and K-feldspar, minor reduction of hematite after at least one year.	

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Table 1 (*continued*)

Work	Sample	Experiment					Analytical Methods	Results	References
		Type.	Temp. (°C)	Pres. (MPa)	Duration	Wet/Dry			
Experimental insights into limestone-hydrogen interactions and the resultant effects on underground hydrogen storage	Single minerals	Static model	30–200 °C	0.1–101 MPa	Till equilibrium is reached	Simulated formation brines (K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, HCO$_3^-$, SO$_4^-$)	PHREEQC	Saturated hydrogen brine almost does not react with silicate and clay minerals. But carbonates (e.g. calcite) can be readily dissolved.	Bo et al. (2021)
	Simulated sandstone samples for two reservoirs	Kinetic model	118/ 56.2 °C	9/5.6 MPa	30/100 years	Simulated formation brines (K$^+$, Na$^+$, Mg^{2+}, Ca^{2+}, Cl$^-$, HCO$_3^-$, SO$_4^-$)	PHREEQC		
Hydrogen-induced calcite dissolution in Amaltheenton Formation claystones: Implications for underground hydrogen storage caprock integrity	Calcite fossils in claystone	Batch-reactor	~25 °C	15 MPa	30 days	10 wt% NaCl brine	SEM; EDX;	Significant dissolution of calcite fossils within caprock samples initiated in intragranular porosity.	Bensing et al. (2022)
Geological hydrogen storage: geochemical reactivity of hydrogen with sandstone reservoirs	Disaggregated sandstones	Batch-reactor	59-80 °C	1–20 MPa	2–8 weeks	NaCl	Pore fluid chemistry; XRD; ICP- Optical Emission Spectroscopy	No changes observed in pore fluid chemistry following experiments.	Hassanpouryouzband et al. (2022)
Modelling hydrogen-rock-brine interactions for the Jurassic reservoir and cap rocks from Polish Lowlands	Reservoir sandstones and caprock claystones/ mudstones	Model	50 °C	12.5 MPa	182–1000 days	Reservoir brine	Geochemists Workbench 11	Geothite and pyrite decomposition and crystallisation of FeO, or FeO and pyrrhotite in sandstones and caprocks. Anorthite decomposition and crystallisation of prehnite and gibbsite in sandstones.	Labus and Tarkowski (2022)
Hydrogen storage in Majiagou carbonate reservoir in China: Geochemical modelling on carbonate dissolution and hydrogen loss	Simulated carbonate reservoir	Kinetic model	120 °C	9.1 MPa	500 years	Simulated formation brine	PHREEQC?	Minor amount of calcite dissolution observed alongside considerable methane generation	Zeng et al. (2022)
Organic-rich source rock/H2/ brine interactions: Implications for underground hydrogen storage and methane production	High TOC marl samples	Batch-reactor	75 °C	10.3 MPa	80 days	Deionised water	GC; XRD; XRF; TOC; SEM; EDX	Trace amounts of methane detected post experiment.	Al-Yaseri et al. (2023b)
Experimental insights into limestone-hydrogen interactions and the resultant effects on underground hydrogen storage	Limestone samples	Batch-reactor	75 °C	9.65 MPa	125 days	3 wt% NaCl brine (pH = 7)	μXCT; NMR; GC	Minor fraction of dissolved calcite in one sample	Al-Yaseri et al. (2023d)
Experimental investigation of shale/hydrogen geochemical interactions	Calcite-rich shale samples	Batch-reactor	75 °C	9.65 MPa	108 days	3 wt% NaCl (pH = 7)	TOC; XRD; SEM; EDX	Precipitation of calcite on shale surfaces due to presence of organic content. No reaction with pyrite observed.	Al-Yaseri et al. (2023c)
Experimental investigation of hydrogen-carbonate reactions via computerised tomography: Implications for underground hydrogen storage	Calcite-limestone and dolomite-limestone sample	Batch-reactor	75 °C	4.83 MPa	75 days	Deionised water	μXCT	Significant calcite expansion. Dolomite dissolution and expansion cancelled out overall change in porosity.	Al-Yaseri et al. (2023a)
Effect of hydrogen on calcite reactivity in sandstone	Calcite	Batch-reactor	105 °C	10 MPa	75 h	Distilled water	Optical microscopy; SEM; EDX; ICP-OES	No evidence of calcite dissolution.	Gelencser et al. (2023)

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Table 1 (*continued*)

Work	Sample	Experiment					Analytical Methods	Results	References
		Type.	Temp. (°C)	Pres. (MPa)	Duration	Wet/Dry			
reservoirs: Experimental results compared to geochemical modelling predictions		Equilibrium model	105 °C	10 MPa	75 h	Water	PHREEQC	Intensive reactions between calcite and H2 resulting in extensive calcite dissolution and methane formation.	Zeng et al. (2023b)
		Kinetic model	105 °C	10 MPa	75 h	Water	PHREEQC	Predicts significant calcite dissolution takes place under H2 pressure, after 27 h the modelled Ca2+ concentration in solution reaches a plateau.	
Role of geochemical reactions on caprock integrity during underground hydrogen storage	Calcareous shale, Siliceous shale, argillaceous shale samples	Kinetic model	72.2 °C	16.9 MPa	30 years	Simulated formation brines	PHREEQC	Calcite reacts with aqueous hydrogen to generate CH4, through reductive dissolution reaction.	

* *Scanning Electron Microscopy (SEM); Energy Dispersive X-ray Spectroscopy (EDX); Electron Microprobe Analysis (EMS); Wavelength-dispersive X-ray (WDX); X-ray Diffraction Analysis (XRD); Inductively Coupled Plasma (ICP); X-ray Fluorescence Spectroscopy (XRF); Micro-x-ray Computed Tomography (μXCT); Specific Inner Surface Area (BET); Total Organic Carbon (TOC); Nuclear Magnetic Resonance (NMR); Gas Chromatography (GC).*

While they are often assumed to remain competent during hydrogen injection and production, their integrity may be altered by geochemical reactions induced by hydrogen storage (Al-Yaseri et al., 2023a). Particularly, reactions that could lead to physical alterations in minerals and pore structure that may change intrinsic properties of the caprock. Although, as these reactions are likely kinetically limited, this may not be relevant across the expected storage timescale (Truche et al., 2013).

3.2. Hydrogen-induced abiotic geochemical reactions

The artificial elevation of hydrogen partial pressure in the subsurface during storage may induce redox reactions, as hydrogen acts as a reducer. Hydrogen can serve as an electron donor for oxidised species present in the pore fluid and host rock mineralogy (Bensing et al., 2022). The kinetics of potential redox reactions are poorly understood, but they are likely kinetically limited due to the high energy barrier required to break the strong, non-polar H—H bonds of hydrogen (436 KJ mol^{-1}) (Truche et al., 2010; Truche et al., 2013; Bensing et al., 2022; Hassan-pouryouzband et al., 2022). Consequently, most abiotic reactions are thought to necessitate extreme reservoir conditions (>100 °C, >15 MPa, >288 g/L salinity) (Perera, 2023). Therefore, most redox reactions are expected to remain insignificant under reservoir conditions representative of UHS, even over storage timescales, provided no catalyst is present (e.g., bacteria, mineral composition and/or surfaces, and engineered material) (Truche et al., 2013). However, it is suggested that at higher temperatures, such as those associated with deep storage reservoirs (60–90 °C), hydrogen may become a more active electron donor and could lead to reactions such as Fe(III) reduction (Didier et al., 2012; Reitenbach et al., 2015), emphasising the importance of suitable site selection.

The injection of hydrogen into the subsurface may impact the geochemical equilibrium of the subsurface as it has the potential to alter key parameters such as pE and pH. pE is a measure of the tendency for a chemical species to acquire or lose electrons; a more negative pE value indicates a more reductive system, as predicted for UHS, as hydrogen is an electron donor (Zeng et al., 2023b). Alternately, pH controls the range of reactions and the dissolution/precipitation of minerals.

Reactions are likely to occur in the interface between stored hydrogen and the residual/displaced pore fluids and/or cushion gas within the pore structure of the reservoir (triple point of the three-phase system; Fig. 2), as dissolution/precipitation reactions require a liquid phase (Flesch et al., 2018). This 'reaction zone' is not regionally defined and will migrate in proximity to the wellbore throughout the storage cycle and may evolve with subsequent cycles. During injection, the interface will move away from the wellbore, and during withdrawal, it will move towards the wellbore (Flesch et al., 2018). It is suggested by Hemme and van Berk (2018) that the most reactive areas may consist of two hotspot regions; the contact area between the reservoir and caprock, and the contact area between the reservoir and underlying rocks, as these areas experience an influx of new material through diffusion over time. Also important is the area surrounding the well, as this will experience significant change of temperature, pressure, and fluid chemistry throughout storage cycles. Therefore, these regions are of particular interest in terms of potential geochemical reactions from hydrogen storage over the lifetime of the reservoir. However, the potential and extent are likely dependent on factors such as mineralogy, brine composition, and operating conditions (temperature, and pressure), and this is poorly understood in the literature, and subject to local variations, requiring further investigation (Bensing et al., 2022; Al-Yaseri et al., 2023b).

3.2.1. Carbonates

Carbonate minerals are commonly found in reservoir and caprocks, with examples including calcite ($CaCO_3$), dolomite ($CaMg (CO_3)_2$), and siderite ($FeCO_3$). These minerals are often major constituents in sedimentary rocks, existing as cement, grains, and matrix. The extents of
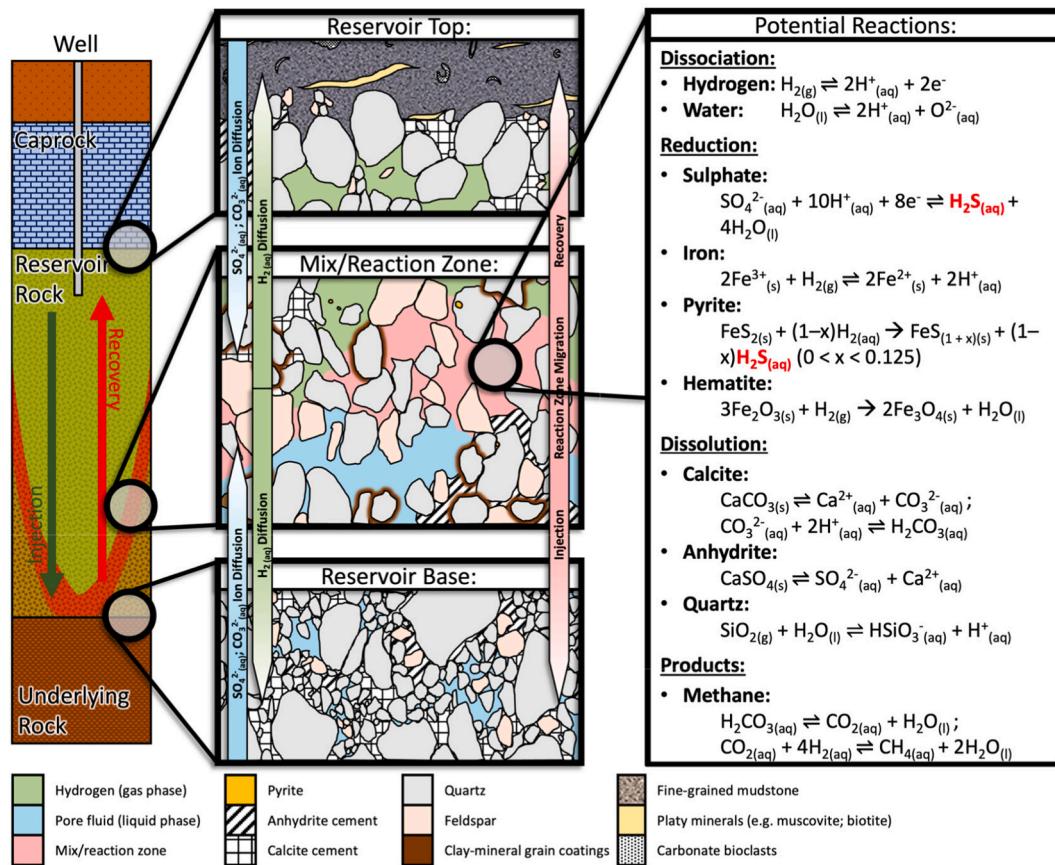
Fig. 2. Potential reactions within the mix zone of a porous reservoir.

This schematic shows a selection of potential reactions that may occur within the mix zone of a hydrogen storage reservoir in porous rocks.

The reaction/mix zone will migrate towards and away from the wellbore depending on the storage cycles (injection and recovery). During injection it will *move away from the wellbore, during withdrawal it will move towards the wellbore. (This image is stretched in the vertical direction and ignores reservoir geometry, such as anticlinal domes).*

New material will diffuse into the reservoir from the surrounding caprock and underlying rocks. These areas are likely hotspot regions for reactions due to the influx of new material preventing lasting equilibrium being developed.

Potential reactions highlighted in the 3rd column may occur, but it is uncertain how energetically favourable they would be at specific reservoir conditions due to an absence of quantitative research.

reactions between carbonates, hydrogen, and brine are poorly understood (Al-Yaseri et al., 2023d), although varying degrees of alteration has been observed experimentally (Flesch et al., 2018; Al-Yaseri et al., 2023d). Carbonate minerals may react with hydrogen ions to produce bicarbonate ions ($CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$). It is also suggested that carbonates may react with hydrogen to produce methane and carbon dioxide ($2\,CO_3^-_{(aq)} + 12H^+_{(aq)} = CH_4_{(aq)} + CO_2_{(aq)} + 4\,H_2O_{(aq)}$), potentially compromising the purity of stored hydrogen (Bo et al., 2021). The presence of calcite in rocks may promote hydrogen dissociation at lower temperatures, leading to calcite dissolution (Al-Yaseri et al., 2023c), which could escalate hydrogen-carbonate reactions through pore fluid acidification. If the pore fluid becomes saturated with carbonate ions, precipitation of carbonate minerals could block pores, reducing porosity and permeability (Pan et al., 2021). Findings from Al-Yaseri et al. (2023d) suggest minimal changes in pore structure in limestones due to reactions between calcite and hydrogenated brine, although this reaction was limited to 78 h so may not be affirmative of what will occur across storage time scales. However, further experiments from the same author demonstrates significant modification in limestone pore networks attributed to observed dissolution and expansion of calcite and dolomite (Al-Yaseri et al., 2023a).

3.2.1.1. Calcite ($CaCO_3$). The impact of hydrogen on calcite remains inconclusive in the literature, the key findings from previous studies are discussed below. Calcite may react with hydrogen ions in pore fluids to produce bicarbonate ions that are soluble in water, leading to mineral dissolution ($CaCO_3_{(s)} + H^+_{(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + HCO_3^-_{(aq)}$) (Al-Yaseri et al., 2023b; Al-Yaseri et al., 2023c), or the formation of carbonic acid ($CaCO_3_{(s)} + 2H^+_{(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + H_2CO_3_{(aq)}$; $H_2CO_3_{(aq)} \rightleftharpoons CO_2_{(aq)} + H_2CO_3^-_{(aq)}$) (Al-Yaseri et al., 2023d). These reactions are unlikely as it relies on the dissociation of hydrogen gas molecules, which does not readily occur. This reaction is believed to be redox dependent as carbonate is reduced by H_2, which increases the pH of the pore fluid, promoting further calcite dissolution (Zeng et al., 2022; Al-Yaseri et al., 2023a; Zeng et al., 2023b).

Geochemical fluid analysis by Hassanpouryouzband et al. (2022) showed no difference in results between experiments run with N_2 (g) as a control and those run with H_2 (g), suggesting an absence of reaction, potentially due to the short reaction time of 2–8 weeks. Batch experiments conducted by Truche et al. (2013) and Gelencser et al. (2023) showed no morphological or chemical evolution of calcite following hydrogen exposure. However, many other studies, such as batch experiments by Flesch et al. (2018) and Bensing et al. (2022), reported dissolution of calcite, which is consistent with models developed by Hemme and van Berk (2018) and Bo et al. (2021) that both predict calcite dissolution. It is important to note that if samples were not pre-equilibrated with the pore fluid used in the examples, could result in calcite dissolution regardless of hydrogen exposure. Studies where

calcite dissolution is observed note significant etching and dissolution of grains, resulting in the formation of staircase structures (Flesch et al., 2018), such as calcite fossil fragments due to their higher internal surface area for reactions, leading to increased intragranular porosity (Bensing et al., 2022). An increase in measured porosity (from 18.55 % to 20.96 %) was recorded by Al-Yaseri et al. (2023d) in calcite-rich limestone samples following 125 days of reaction at 75 °C and 9.65 MPa hydrogen partial pressure. As these results come from relatively short-duration laboratory experiments, it is likely equilibrium has not been reached, leading to over emphasise on dissolution steps of reactions. One study also observed calcite precipitation on shale surfaces after hydrogen exposure (Al-Yaseri et al., 2023c), although this has not been reported elsewhere in the literature.

Contrary to this, calcite expansion has also been observed in the literature, and in some cases, it is more prominent than calcite dissolution, leading to a reduction of effective porosity of up to 47 % (Al-Yaseri et al., 2023a). The mechanism is thought to be due to hydrogen diffusion through the solid calcite phase resulting in volume expansion (Al-Yaseri et al., 2023a). This can restrict pore spaces and block pore throats, hence decreasing the effective porosity, although this phenomenon has not been reported elsewhere in the literature.

3.2.1.2. Dolomite (CaMg (CO$_3$)$_2$). Interactions between hydrogen and dolomite have not been extensively investigated, despite dolomite being a common cement mineral, therefore the behaviour of dolomite in UHS situations remains inconclusive pending further investigation. Studies that have included dolomite yield conflicting results, but dissolution is predicted, similar to other carbonate minerals: $4H_{2\ (g)} + CaMg\ (CO_3)_{2\ (s)} \rightleftharpoons CaCO_{3\ (s)} + Mg\ (OH)_{2\ (s)} + CH_{4\ (g)} + H_2O\ _{(l)}$ (Al-Yaseri et al., 2023a). In batch reactions by Truche et al. (2013), dolomite remained unaltered even at 30 bar hydrogen partial pressure, as SEM analysis showed no morphological evolution of minerals surface. However, modelled results from Hemme and van Berk (2018) predict dolomite precipitation in reservoir rocks. Dolomite dissolution was observed in Al-Yaseri et al. (2023a); however, the effects on porosity were effectively cancelled out by grain expansion effects, like those observed with calcite.

3.2.2. Clay minerals

Clay minerals are extremely fine-grains, less than 4 μm, compositionally phyllosilicates that contain variable amounts of iron, magnesium, alkali metals, and other common cations in sheet-like structures. They are major contributors to the bulk rock specific surface area and the ultrafine nano-pore portion of the pore network in sedimentary rocks. The fine grain size and tortuous pore network formed by clay minerals are responsible for the ultralow permeability of clay-rich mudstones (Ziemianski and Derkowski, 2022).

It is possible that ferric ions (Fe^{3+}) present in clays may be reduced to ferrous ions (Fe^{2+}) through the following reaction: $2Fe^{3+}\ _{(s)} + H_{2\ (g)} \rightleftharpoons 2\ Fe^{2+}\ _{(s)} + 2H^+$ (Didier et al., 2012). The reduction of iron by hydrogen is known to be strongly dependent on temperature, pressure, and reaction times, so it is important to evaluate its extent at conditions relevant to UHS (Didier et al., 2012). Further to this, it is suggested that hydrogen adsorption may occur between hydrogen and clay minerals (Didier et al., 2012). Experiments by Didier et al. (2012) concluded no evidence of Fe^{3+} reduction at reservoir conditions; this agrees with results from simulated batch reactions by Bo et al. (2021) that show no evidence of any reaction taking place between clay minerals and hydrogen. However, they did observe that Callovo-Oxfordian clay samples can adsorb 0.05 wt% hydrogen at 90 °C, a relevant temperature for storage. This is thought to be principally physiosorption, likely caused by van der Waals inteactions on the clay's surface, and therefore does not constitute a geochemical reaction. Due to a higher pressure in the subsurface, a significant portion of hydrogen could be physiosorbed into available micropores of clay minerals that have been proven to control gas adsorption properties of rocks (Perera, 2023; Ziemianski and Derkowski,

2022). The density of adsorbed hydrogen is double that of free hydrogen gas, meaning clays can increase the gas storage capacity of rocks; however, this may also lead to minor hydrogen trapping (Ziemianski and Derkowski, 2022).

Hydrogen sorption to clay minerals can lead to swelling-induced stress changes (Heinemann et al., 2021). The amount of clay swelling is directly related to the water content of the clay minerals, with no swelling seen in fully dry or fully saturated clays (Heinemann et al., 2021). Clay swelling may lead to fracture closing but also swelling-induced critical stressing of faults leading to slip (Heinemann et al., 2021). However, recent results from a British Geological Survey experiment showed the removal of grain-coating clays (British Geological Survey - The University of Manchester, 2023), and models by Hemme and van Berk (2018) showed the dissolution of illite and precipitation of kaolinite. Further models by Zeng et al. (2023b) showed various degrees of clay mineral dissolution (kaolinite 0.0358 %; smectite 0.0114 %; and illite 0.00005 % of the total amount of mineral present) and concluded that dissolution is accelerated in more alkaline conditions produced by the concurrent redox reactions occurring between hydrogen and carbonates. Further studies regarding the behaviour of clay minerals during hydrogen exposure are therefore necessary to provide supporting experimental evidence and clarity to the tentative conclusions given in the literature.

3.2.3. Sulphates

Sulphate minerals contain the SO_4^{2-} ion within their structure and are common in evaporitic depositional environments, appearing as anhydrite ($CaSO_4$), baryte ($BaSO_4$), and gypsum ($CaSO_4.2H_2O$). When sulphate, acting as an electron acceptor, interacts with hydrogen ions it may undergo reduction, producing hydrogen sulphide ions and water according to the reaction: $SO_{4\ (aq)}^{2-} + 9H_{(aq)}^+ + 8e^- \rightleftharpoons HS_{(aq)}^- + 4H_2O\ _{(aq)}$ (Reitenbach et al., 2015; Hemme and van Berk, 2018; Al-Yaseri et al., 2023c). This reaction poses challenges for underground hydrogen storage because hydrogen sulphide is corrosive and can degrade subsurface infrastructure, as well as the purity of the stored hydrogen, leading to costly hydrogen cleaning on production. Therefore, sulphates are an important group of minerals warranting focussed research.

3.2.3.1. Anhydrite (CaSO$_4$). Both experimental and modelled results have demonstrated the dissolution of anhydrite. Observations by Flesch et al. (2018) depict various stages of anhydrite dissolution, showing staircase structures and edge-pit development in pyramidal formations (see Fig. 3E). These findings are consistent with modelled results, where anhydrite was consumed within the system (Hemme and van Berk, 2018). If complete dissolution does occur, the intrinsic properties of the reservoir will be altered, with the extent depending on the quantity of anhydrite present. Extensive dissolution could significantly increase porosity, yet the production of hydrogen sulphide gas as a by-product could greatly diminish the quality of stored hydrogen and introduce risk to wellbore infrastructure. However, in evaporitic successions, such as those utilised in cavern storage, no interactions between hydrogen and anhydrite have been reported, likely due to the absence of water. This lack of interaction may be attributed to the limited number of caverns currently in operation for hydrogen storage. Nonetheless, it could emerge as a concern with the further development of these techniques, leading to the utilisation of bedded evaporite formations containing higher proportions of insolubles such as anhydrite.

3.2.3.2. Gypsum (CaSO$_4$.2H$_2$O). Gypsum has received limited attention in the literature, despite its compositional similarities with anhydrite. This lack of investigation may stem from the literature's primary focus on hydrogen interactions with reservoir rocks, rather than caprocks that may contain higher amounts of gypsum within evaporite formations. Studies by Hassanpouryouzband et al. (2022) revealed no difference in geochemical fluid analysis between control experiments with $N_{2\ (g)}$ to
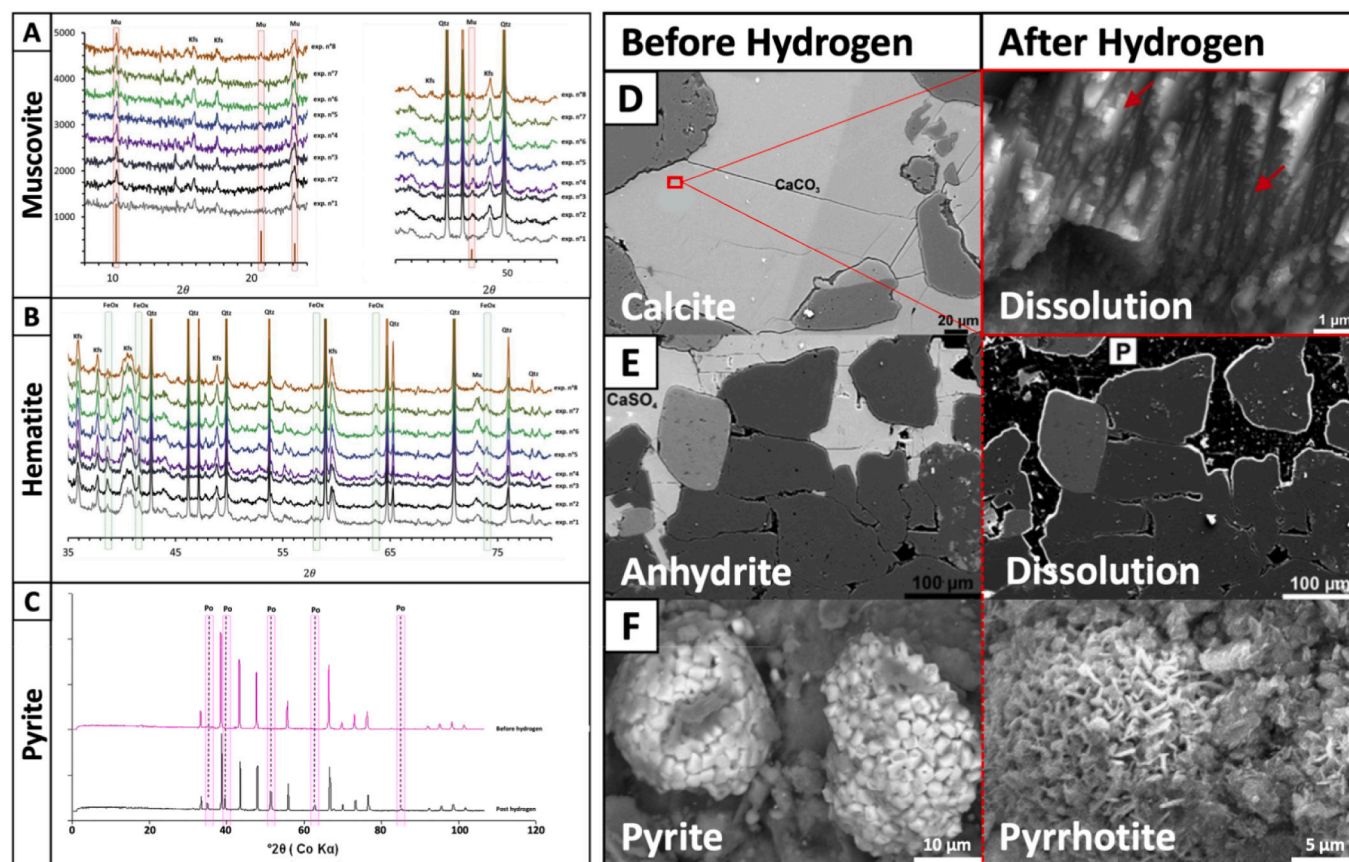
Fig. 3. Experimental evidence of mineral alteration due to hydrogen exposure.

X-ray Diffraction Results pre- and post- *hydrogen experiment: (left)*

A) Evolution of XRD peaks of muscovite in experimental products from the reference (exp. No1). This shows an increase in the muscovite peak intensities in experimental products suggesting a small but recognisable reaction has taken place (100-200 °C, 10 MPa, 1.5–6 months) (Yetka et al., 2018); B) Evolution of XRD peaks of hematite in experimental products from the reference (exp. No1). This shows an increase in the hematite peak intensities in experimental products suggesting a small but recognisable reaction has taken place (100-200 °C, 10 MPa, 1.5–6 months) (Yetka et al., 2018); C) XRD peaks for pyrrhotite (Po) are only present in the experimental sample, alongside some retained peaks for pyrite from the starting sample (90-180 °C, 0–1.8 MPa, 300 h) (Truche et al., 2010).

SEM Image Results pre- *and post- hydrogen experiment: (right)*

*D) SEM BSE image of calcite prior to hydrogen exposure and post-hydrogen exposure (<40 °C, 10–20 MPa, ~6 weeks) showing dissolution through staircase structures (Flesch et al., 2018); E) SEM images of anhydrite prior to hydrogen exposure and post-hydrogen exposure (<40 °C, 10–20 MPa, ~6 weeks) showing the complete removal of anhydrite cement replaced by large pore spaces (Flesch et al., 2018); F) SEM image (BSE) of framboidal pyrite naturally present in claystone sample before and after exposure hydrogen (90 °C, 0.6 MPa, 150 h – 3 months), strong alteration is visible as initial cubic structures are replaced with needle-like crystals of pyrrhotite (Truche et al., 2013). A & B: Adapted from Yetka et al. (2018) with permission, © Elsevier 2018; C: Adapted from Truche et al. (2010) with permission, © Elsevier 2010; D & E: Adapted from Flesch et al. (2018) with permission, © Elsevier 2018; F: Adapted from Truche et al. (2013) with permission, © **Elsevier 2013.***

those with $H_2{}_{(g)}$ suggesting an absence of geochemical reactions. As these conclusions are based on fluid analysis, they do not rule out the possibility of minor reactions that can only be observed through higher resolution compositional and microstructural analysis of the sample post-hydrogen exposure.

3.2.3.3. Baryte ($BaSO_4$). Baryte has not been extensively studied in experimental research, indicating either a lack of investigation or its perceived insignificance as a potential mineralogical constituent. Nevertheless, baryte serves as a common diagenetic cement in the UK Sherwood Sandstone, a principal aquifer and a potential host for porous storage of hydrogen (Mouli-Castillo et al., 2020). Models presented by Hemme and van Berk (2018) suggest that the reactive amount of baryte is completely consumed within the reference scenario, but this is not observed elsewhere. This highlights the need for further investigation to comprehensively understand interactions between hydrogen and baryte in subsurface environments, to confirm the lack of reactivity.

3.2.4. Silicates

Silicates are characterised by the SiO^{4-} ion in their mineral structure and constitute the majority of rocks on Earth due to their stability and relative resistance to alteration. They are common components of reservoirs and caprocks, existing as grains and cements such as quartz (SiO_2), K-feldspar ($KAlSi_3O_8$), and muscovite ($KAl_3Si_3O_{10}(OH)_2$). Experimental observations (e.g., Flesch et al., 2018; Yetka et al., 2018) and models (e.g., Bo et al., 2021), generally agree that silicates such as quartz, K-feldspar, and mica remain unaltered when exposed to hydrogen. SEM images show no textural changes indicative of mineralogical transformations in silicates before and after experiments (Yetka et al., 2018), suggesting that the bulk composition of most reservoir sandstones (dominated by silicates) undergo no significant modification upon hydrogen exposure.

3.2.4.1. K-Feldspar ($KAlSi_3O_8$). Batch-reaction experiments and geochemical fluid analysis reveal no changes to K-feldspar following exposure to hydrogen, as confirmed by SEM images (Yetka et al., 2018; Hassanpouryouzband et al., 2022). Simulated batch-reactions also

indicate the stability of K-feldspar during hydrogen exposure (Yetka et al., 2018). Models by Hemme and van Berk (2018) predict some K-feldspar precipitation in reservoir rocks, although this has not been observed experimentally so its potential remains unclear.

3.2.4.2. Muscovite (KAl$_3$Si$_3$O$_{10}$(OH)$_2$). In contrast to other silicate minerals, experimental data suggests minor alteration of muscovite following exposure to hydrogen. Batch-reactions demonstrated an increase in muscovite XRD peak intensities relative to pre-experiment references, indicating a small but detectable compositional change in the starting sandstone due to hydrogen exposure (Fig. 3A) (Yetka et al., 2018). This finding challenges the notion that silicates are inert to alteration and indicates a need for further investigation where sandstone targets are rich in muscovite.

3.2.4.3. Quartz (SiO$_2$). Experimental results show no alteration of quartz (Truche et al., 2013; Flesch et al., 2018; Yetka et al., 2018; Al-Yaseri et al., 2023c; Zeng et al., 2023a), consistent with modelled results (Yetka et al., 2018; Bo et al., 2021). Indicating the stability of quartz-rich reservoir and caprock formations.

3.2.5. Iron-oxides

Iron oxides are presumed to play a significant role as a redox reaction partner for hydrogen during UHS, given its common occurrence in various oxidised forms in the subsurface. Iron-oxides, consequently, have the potential to be reduced in the presence of hydrogen, leading to the mobilisation of iron that may subsequently precipitate elsewhere.

3.2.5.1. Hematite (Fe$_2$O$_3$). In batch-experiments conducted by Yetka et al. (2018), it was anticipated that hematite would be reduced to magnetite during exposure to hydrogen, as predicted through simulated equilibrium experiments (Yetka et al., 2018). The model predicted a decrease in hematite concentrations from approximately 3.5 wt% to 1.24–2.48 wt% following the equilibrium reaction, where Fe^{3+} in hematite is progressively reduced to Fe^{2+} in magnetite. The most probable mechanism proposed is: $3\,Fe_2O_3\,_{(s)} + H_2\,_{(g)} \rightleftharpoons 2\,Fe_3O_4\,_{(s)} + H_2O\,_{(l)}$ (Yetka et al., 2018). However, experimental data did not align with these predictions, as hematite was identified through XRD as the only iron-oxide present after exposure to hydrogen. This is consistent with SEM analysis, which showed no mineralogical alterations. However, there were intensity increases in diagnostic XRD peaks for hematite in several experiments (Fig. 3B), suggesting that a small but detectable reaction did occur. But detailed information is lacking to interpret these results and identify a specific mechanism, indicating the need for further study.

3.2.6. Iron-sulphides

Similarly to iron-oxides, iron-sulphides can form an important redox reaction partner with hydrogen in the subsurface. However, reactions may mobilise sulphide alongside iron, which can react with hydrogen to form hydrogen sulphide leading to a reduction in quality of the stored hydrogen and the need for post-production processing of hydrogen. This could add costs and time to storage operations and could potentially limit uses for stored hydrogen if high purities are required.

3.2.6.1. Pyrite (FeS$_2$). The influence of hydrogen exposure on pyrite is one of the most well-studied among all mineral-hydrogen reactions, with the reduction of pyrite to iron-monosulphides (e.g., pyrrhotite; $2FeS\,_{(s)} \rightleftharpoons Fe^{2+}\,_{(aq)} + 2e^-$ (Al-Yaseri et al., 2023c)) subject to extensive experimental investigation. This reaction is thought to be likely at temperatures associated with UHS (Truche et al., 2013; Reitenbach et al., 2015). Even at low concentrations (<0.1 wt%), there is sufficient pyrite present for abiotic reduction to take place, associated with considerable amounts of hydrogen sulphide production (Reitenbach et al., 2015). As previously mentioned, hydrogen sulphide may alter pore fluid chemistry through acidification, ultimately leading to the

deterioration of hydrogen purity (Truche et al., 2013; Hassanpour-youzband et al., 2022). Preliminary evidence of pyrite reduction from analysis by Truche et al. (2010) showed initial XRD patterns with only well-developed pyrite peaks, but following hydrogen exposure, small pyrrhotite peaks had developed (Fig. 3C). This was further investigated by Truche et al. (2013), where the reaction was imaged, showing that initially cubic pyrite framboids were replaced by needle-like crystals of pyrrhotite (Fig. 3F). It is important to note that these experiments were performed at temperatures >90 °C, which is above the temperatures expected for many potential UHS reservoirs.

This reaction is characterised by a coupled dissolution-precipitation mechanism occuring at the pyrite-pyrrhotite interface rather than solid-state transformation (Truche et al., 2010; Truche et al., 2013). This means the reaction involves both pyrite dissolution and pyrrhotite precipitation alongside hydrogen and hydrogen sulphide diffusion through the following mechanism (Truche et al., 2010): $FeS_2\,_{(s)} + (1–x)\,H_2\,_{(aq)} \rightleftharpoons FeS_{(1+x)}\,_{(s)} + (1–x)\,H_2S\,_{(aq)}$ (0 < x < 0.125). This is evidenced texturally as pyrrhotite crystallites grow perpendicular to the sharp reaction front, with the size of pyrrhotite crystallites increasing from the pit surface to the reaction front (geodic texture). Furthermore, the pyrrhotite is porous and chemically homogeneous, so it is unlikely to have been formed via solid-state transformations, which result in structural gradients and non-porous dense phases (Truche et al., 2010). The reaction rate is therefore controlled by both pyrite reductive dissolution and pyrrhotite precipitation, as well as sulphide diffusion through the porous pyrrhotite microstructure (Truche et al., 2010). With pyrite solubility controlling the rate and extent of reaction at <150 °C and hydrogen partial pressure < 0.6 MPa, and pyrrhotite precipitation controlling the reaction at higher temperatures and pressures (Truche et al., 2013). Extents of reactions have been investigated through modelling, showing that higher pH values, temperature, and hydrogen partial pressures all lead to more pyrite dissolution.

Results from Hassanpouryouzband et al. (2022) batch reaction experiments disagree with this, as no differences in fluid composition were found between those run with a hydrogen atmosphere compared to those with a nitrogen atmosphere, suggesting an absence of geochemical reactions. However, this seems unlikely considering all the textural and geochemical evidence presented by Truche et al. (2010). The fluid analysis used by Hassanpouryouzband et al. (2022) may not show changes as it is a coupled dissolution-precipitation reaction, so the fluid does not become enriched in new material. Experiments by Bensing et al. (2022) also noted no pyrite reduction during hydrogen exposure, but this is likely due to the low temperatures used (less than 25 °C as outlined by (Truche et al., 2013)).

3.3. Summary on the reactive mineralogies in hydrogen storage

Limited mineralogical transformations have been identified in the literature, but it is likely that hydrogen does influence the geochemistry of the subsurface, potentially causing reactions to occur in the reservoir and caprock during hydrogen storage (as depicted in Fig. 4 and summarised in Table 2). Quartz, a main constituent of many target reservoir formations and caprocks, does not react with hydrogen. Geochemical modelling suggests some mineral alteration is expected in reservoir rocks as the system equilibrates to elevated hydrogen concentrations present during storage cycles (Hemme and van Berk, 2018; Yetka et al., 2018). Somewhat conclusive results show that UHS can lead to the dissolution of carbonates, sulphates (anhydrite), and pyrite, as well as the precipitation of pyrrhotite, depending on the host-rock mineralogy.

In assessing geochemical reactions for UHS, it is critical to distinguish between reactions expected on engineered storage timescales (10–100 years) and those occurring over geological timescales (10^5–10^6 years). Laboratory studies provide insight into likely reaction rates and models can help to predict their extent on storage timescales, although detailed discussion and consensus is lacking in the literature. Pyrite reduction has been shown to occur within 150 h to 3 months by Truche
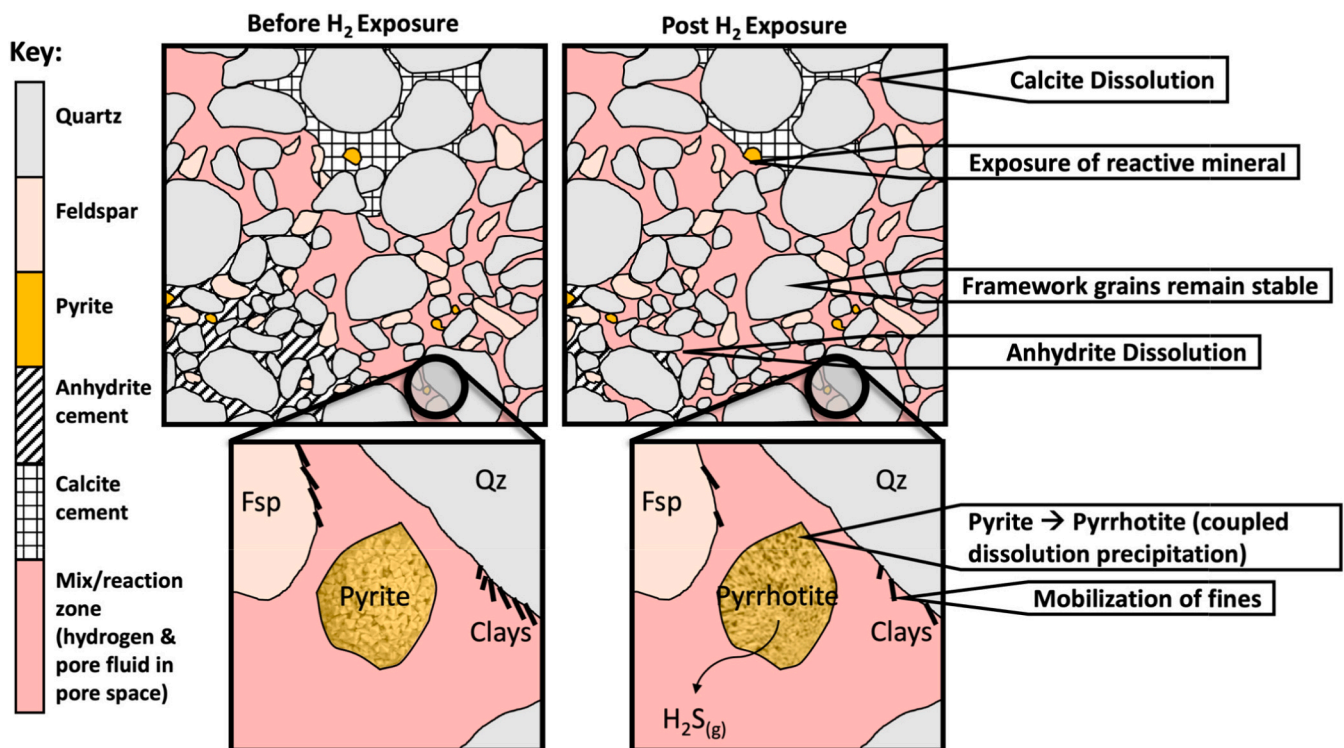
Fig. 4. Evaluation of expected hydrogen induced mineral reactions.
Schematic illustration of the reactions that occurred in a before and after comparison.
On the left: the partial dissolution of pore-filling minerals is shown, which goes along with an increase in porosity but no effect on permeability.
On the right: partial and complete dissolution of pore-filling cements, which relates to an increase in porosity, permeability and measured specific subsurface area.

et al. (2010) and Truche et al. (2013) under storage conditions, suggesting it could impact storage quality over operational timescales by forming H₂S gas. Experimental results have also indicated calcite, and sulphate may begin dissolving within 30 days – 6 weeks at reservoirs temperatures and pressures, potentially altering porosity in UHS reservoirs (Flesch et al., 2018; Bensing et al., 2022). In contrast, reactions with silicates, particularly quartz and feldspar, have not been observed within relevant timeframes (Yetka et al., 2018), indicating stability over UHS timescales. These findings highlight the importance of focusing on reactions like pyrite reduction and carbonate dissolution in predicting UHS storage impacts, as these reactions may reach observable extents within typical operational lifespans.

It is known that hydrogen has a major impact on sulphur chemistry, with pyrite reduction being the main abiotic geochemical reaction induced by hydrogen exposure. If extensive, dissolution reactions may alter the intrinsic properties of rocks such as porosity and permeability, thereby changing the storage capability and reservoir performance of the UHS site. This is likely mitigated by the abundance of unreactive minerals typically found in many sandstones (silicates: quartz, K-feldspar) that will remain stable during hydrogen exposure. The exception to this is muscovite, which may undergo minor recrystallisation, demonstrating silicate phases can be altered by interactions with hydrogen (Yetka et al., 2018).

The effects of acidification on reservoir rocks and fluids are widely reported in literature surrounding CCUS (e.g., (Pudlo et al., 2015)). Therefore, many reactions may be dependent on the dissociation of hydrogen into H^+ ions that will decrease the pore fluid pH, resulting in alterations, as pH has a great influence on rates and extents of reactions. For example, alkaline conditions promote pyrite-pyrrhotite reduction at temperatures and pressures relevant to UHS (Truche et al., 2013), whereas acidic conditions favour carbonate dissolution (Bo et al., 2021). Dissolution can then promote further contact between hydrogen and reactive minerals that were not originally exposed to hydrogen.

However, hydrogen has a very low solubility in water, and therefore the production of H^+ ions will be severely limited.

The mechanism of many mineralogical transformations have not been clearly identified in the literature, and therefore further investigation is justified to gain a better understanding of the potential for mineral-hydrogen interactions. Ideally, these studies should examine the effects at longer time scales (e.g., >6 months) at temperatures likely to be reached in storage scenarios to investigate reactions in relation to seasonal storage.

It is also unknown how engineered components such as steel and cement will influence abiotic reactions in the near-wellbore environments (Reitenbach et al., 2015). It is also important that future studies use temperature and pressure ranges relevant to UHS. High-temperature conditions may accelerate reactions, but they can also alter mineralogy and pore structure, and high pressure can increase the adsorption properties of clay minerals (Al-Yaseri et al., 2023c). This means results cannot be certain to have been produced solely through reactions with hydrogen.

3.4. Implications for UHS efficiency and security

The level of influence geochemical reactions have on the integrity of reservoirs and caprocks remains uncertain, yet it is likely mitigated by the stability and inertness of predominant minerals like quartz in siliciclastic reservoirs. While dissolution can enhance reservoir porosity and storage capacity, it may compromise the sealing ability of the caprock, conversely, precipitation can reduce permeability through pore clogging, enhancing caprock properties but reducing reservoir storage efficiency. The variability in the effects of hydrogen on rocks, as observed in studies by Flesch et al. (2018), who highlight the need for accurate predictions on a case-by-case or individual reservoir bases. Moreover, changes in chemical environment can trigger various fluid-assisted grain-scale processes, potentially leading to permanent

Table 2
Evaluation of potential hydrogen induced mineral reactions.

Mineral Group	Mineral Phase	Reaction	Evidence	Likelihood of reaction
Silicates	**K-feldspar**	**None**	No evidence to support any changes (Yetka et al., 2018; Bo et al., 2021)	**No likelihood of reaction**
Silicate	**Quartz**	**None**	No evidence to support any changes (Yetka et al., 2018; Bo et al., 2021)	**No likelihood of reaction**
Carbonates	**Calcite**	**Likely**	Different stages of calcite alteration through staircase structures imaged, as well as agreement in models (Flesch et al., 2018; Bo et al., 2021; Bensing et al., 2022)	**Medium likelihood of reaction** due to abundance of calcite cement in reservoir and cap rock.
Carbonate	**Dolomite**	**None**	Some evidence of dolomite expansion and dissolution altering the pore network (Al-Yaseri et al., 2023a)	**Medium likelihood of reaction** due to the abundance of dolomite cement in reservoir and cap rock.
Clay Minerals	**Iron-bearing clays**	**Likely**	Fe^{3+} is not reduced to Fe^{2+} at conditions representative of UHS, but hydrogen adsorption into clay structure does happen (Didier et al., 2012)	**Medium likelihood of reaction** as changes to clay structure can influence porosity and permeability, and adsorption of hydrogen can promote dissociation the H^+ ions which may go on to cause more reactions
Silicate	**Muscovite**	**Likely**	Changes in XRD peaks suggesting minor but detectable compositional changes, although uncertain of mechanism (Yetka et al., 2018)	**Medium likelihood of reaction**, it is evidence that silicates can be affected by hydrogen exposure
Iron-oxides	**Hematite**	**Likely**	Changes in XRD peaks suggesting a minor but detectable compositional change, suggested by modelling as hematite dissolution leading to magnetite precipitation (Yetka et al., 2018)	**Medium likelihood of reaction** however, the reaction is minor, and the mineral does not account for much of the composition of reservoir or cap rocks. This reaction is likely kinetically limited under reservoir conditions.
Sulphate	**Anhydrite**	**Very likely**	Evidenced in experimental and modelled results with different stages of anhydrite	**High likelihood of reaction** as complete dissolution of pore filling anhydrite has

Table 2 (*continued*)

Mineral Group	Mineral Phase	Reaction	Evidence	Likelihood of reaction
			alteration imaged (Flesch et al., 2018)	been observed under reservoir conditions.
Iron-sulphides	**Pyrite**	**Very likely**	Pyrite is reduced to pyrrhotite (coupled dissolution-precipitation) at conditions representative of UHS as seen in SEM images and XRD analysis (Truche et al., 2010; Truche et al., 2013)	**Very high likelihood of reaction** due to production of $H_2S_{(g)}$, which is corrosive, toxic, and pollutes the stored hydrogen leading to costly post-processing of the gas. This reaction is confirmed to occur under reservoir conditions.
Sulphates	**Baryte**	**Unsure**	Modelled results suggest reactive amounts of baryte will be consumed, but there is no further evidence in the literature	**Medium likelihood of reaction** depending on the quantity of baryte in host rock
Sulphate	**Gypsum**	**Unsure**	Suggested to have no reaction through geochemical analysis of pore fluid, but not enough evidence for a definitive answer	**Medium likelihood of reaction** depending on the amount of gypsum in the host rock (could be higher for cap rocks)

deformation (e.g., local grain-contact cement dissolution, clay-mineral sorption/desorption with grain boundaries, fluid-assisted slow crack growth, mineral dissolution/precipitation, and/or fractional slip) (Heinemann et al., 2021). This has the potential to induce time-dependent creep deformation within the reservoir, thereby impacting fault stability (Heinemann et al., 2021).

Dissolution of carbonates and sulphate minerals is important as it may lead to mechanical weakening of the reservoir, particularly in rocks containing carbonate/sulphate-cemented faults. Dissolution of pore-filling cements may also cause mobilisation of finer grain fractions, e. g., clay minerals that were initially trapped in the rock matrix prior to hydrogen exposure, further causing pore-clogging if accumulation occurs in pore throats. Although flow rates are only likely to be significant in the near-wellbore region. If carbonate expansion is shown to occur under UHS conditions it may significantly alter pore networks by block pore throats and spaces, causing the reservoir to become less porous and permeable, thus less efficient for cyclic storage. As this phenomenon has only been observed in on study (Al-Yaseri et al., 2023a), further investigation is required to assess the suitability of carbonate-rich reservoirs as UHS hosts and determine the mechanism leading to the observed calcite expansion. This is of particular concern in regions investigating hydrogen storage in carbonate reservoirs, such as Western China, and parts of the Middle East (Zeng et al., 2022).

Caprocks may be less affected by hydrogen storage due to their tight nature; hydrogen is not expected to permeate through them easily, even under increased stress and direct contact from extreme buoyancy. In unfaulted caprocks, hydrogen is likely to enter predominantly through diffusion, a very slow process that is unlikely to result in significant hydrogen migration over storage timescales (Hemme and van Berk, 2018). The effective diffusion coefficient for hydrogen in water-saturates caprock is estimated as $3.0 \times 10^{-11} \, m^2 s^{-1}$, meaning that substantial diffusion over the storage period is unlikely. The potential for

specific mineral reactions within underground hydrogen storage (UHS) largely depends on the distribution and abundance of reactive minerals within both reservoir and caprock formations. For example, reactions with pyrite and other sulphide minerals—potentially leading to hydrogen sulphide formations—are more likely to occur in caprock environments where these minerals are prevalent. However, since hydrogen availability in caprock is mainly controlled by diffusion, these reactions are expected to be minimal over typical storage durations. Consequently, the likelihood of significant reactions due to hydrogen diffusion with caprocks remains low, even though the mineralogy of caprocks may otherwise promote such reactions.

Silicate-dominated reservoirs, such as quartz-rich sandstones, are likely to be the most stable as dissolution of more reactive minerals is unlikely, reducing major impact on reservoir integrity. Reservoirs and caprock formations low in clay minerals are less likely to be compromised by dissolution and mobilisation of finer-grained material, minimising the risk to changes in porosity and permeability throughout storage. Due to the large potential storage volumes that porous rocks represent, any alterations to intrinsic properties may be naturally mediated throughout the large size of the reservoir. For example, pore-clogging may occur in some locations, reducing pore space, but dissolution may occur elsewhere, increase pore space (Flesch et al., 2018). Therefore, overall changes in porosity and permeability at the macro-scale may be buffered by different effects on the microscale.

3.5. Suggestions for future experimental design

Interest ion underground hydrogen storage in porous reservoirs is on the rise, yet there remains limited literature concerning its influence on abiotic geochemical reactions. Relevant research is confined to a handful of published experimental data (e.g., Truche et al., 2010; Truche et al., 2013; Berta et al., 2018; Flesch et al., 2018; Yetka et al., 2018; Hassanpouryouzband et al., 2022) and preliminary modelling (e.g., Hemme and van Berk, 2018; Bo et al., 2021). Some of these studies are related to radioactive waste disposal, featuring storage conditions from those expected with UHS. For instance, experimental temperatures in these studies can reach up to 250 °C, whereas UHS is anticipated to operate within the range of 50–100 °C (Yetka et al., 2018). The available literature fails to clarify the potential for reactions over relevant storage time scales of 10s of years for hydrogen storage, and the mechanisms/kinetics of these reactions remain poorly understood (Yetka et al., 2018). Furthermore, there is a notable disparity among authors regarding whether no reactions occur or whether they are significant enough to impact UHS reservoir operation (e.g., (Hassanpouryouzband et al., 2022)). Others argue that further studies are necessary to quantify the rates and extents of reactions expected during UHS (e.g., Truche et al., 2013; Yetka et al., 2018; Flesch et al., 2018). Currently, there is little quantitative analysis on geochemical reactions concerning temperature and pressure relevant to the expected storage conditions across a variety of host rock mineralogies. This leads to an inconclusive understanding of the implications for hydrogen loss and reservoir integrity. Further investigation is therefore imperative, as the lack of consensus poses a risk to the implementation of UHS and investor/societal confidence.

To ensure that experimental results can be related to potential in-situ bedrock behaviour, future experiments should test rocks under specific reservoir conditions and timescales to improve accuracy and understanding of potential hydrogen interactions. For instance, further experimental work should focus on clarifying the effects of hydrogen exposure on different mineral phases to replicate field conditions (including fluid chemistries) and support the development of more realistic models. Additionally, thorough characterisation of potential reservoir and caprock formations through the integration of multiple techniques is essential to generate representative models of UHS stores. This multiscale and multi-technique approach is necessary for comparing pre- and post- experimental datasets to increase confidence in conclusions regarding the effect of hydrogen on the subsurface.

Measurements of porosity and permeability can be conducted directly, such as through helium porosimetry, or through imaging techniques like microscopy or computer tomography, which offer the advantage of revealing internal structure in a non-destructive way.

It's important to note that utilising hydrogen in laboratory experiments presents various health and safety challenges due to its reactive and flammable nature, which can be a significant barrier to further study. Risks can be mitigated by using suitable procedures, monitoring equipment, and materials, such as 316 stainless stell (high Mn, < 13 % Ni) to decrease the susceptibility of hydrogen embrittlement and blistering of pressure reactors (Hassanpouryouzband et al., 2022). Consideration of the Joule-Thomson effect relating to rapid heating of vessels during hydrogen injection can also de-risk some experiments.

Experiments should also investigate the implications of other constituent fluids in the subsurface, such as organic content (e.g., oil and gas in depleted reservoirs). Interactions between injected hydrogen and organic matter of cap- and reservoir rock have the potential to generate CH_4 (g) and H_2S (g), but this is rarely evaluated in the literature (Al-Yaseri et al., 2023b). This includes the potential for hydrogen trapping through adsorption on kerogen in micropores in high organic content shales, leading to the expulsion of methane (Al-Yaseri et al., 2023b). Experimentation showed traces of methane in GC analysis following shale reaction with hydrogen at 1500 psi, 75 °C over 80 days (Al-Yaseri et al., 2023b). This suggests that a reaction occurs, most likely the oxidation of hydrogen and simultaneous reduction of organic content. However, the extent of this reaction is probably constrained by the experimental conditions due to the relatively low temperatures and reaction time; reactions may be more extensive over longer storage cycles (Al-Yaseri et al., 2023b). Additionally, during organic content oxidation, the release of CO_2 may lead to the deposition of calcite, resulting in a pH increase in storage rocks (Al-Yaseri et al., 2023c).

While this review centers on abiotic geochemical reactions within UHS, the role of microbial activity in subsurface environments could potentially impact hydrogen storage security. Microbial processes may catalyze reactions that otherwise progress slowly, particularly in reservoirs containing organic matter. For example, sulphate-reducing bacteria (SRB) can metabolize hydrogen to produce hydrogen sulphide (H_2S), which would alter both the pore fluid chemistry and hydrogen purity (Reitenbach et al., 2015). Microbial biofilms could also modify reservoir properties by clogging pore spaces, thereby reducing permeability. Although microbial effects are not the focus here, future studies exploring UHS storage should consider the potential for microbial catalysis in regions with active microbial populations or organic-rich deposits.

It is crucial that temperatures and pressures used in experiments are relevant to UHS, as reactions are likely to occur more rapidly at higher temperatures. Additionally, it is essential that all three phases (rock, pore fluid, hydrogen) are present in these experiments. The pore fluid phase is essential when studying the geochemical reactions as experiments using dry hydrogen alone have not led to any reactions (Bensing et al., 2022). Even though this makes the experimental design more complex as treating mudstones with brine can often lead to disintegration and swelling of clay minerals. This is especially relevant where legacy samples are used that have been allowed to desiccate and/or become structurally weak. Finally, as well as experiments, more models are needed to comprehensively demonstrate the effects of hydrogen on mineralogy at timescales not replicable in the laboratory environment but more relevant to seasonal hydrogen storage. However, care must be taken to ensure results from models are realistic. Models that assume the system can reach thermodynamic equilibrium often lead to an overestimation of changes in mineral volumes and gas conversion (Zeng et al., 2023b). Kinetic models therefore provide more likely results, but it is also suggested that the classical thermodynamic approach for aqueous redox reactions overestimates the reactivity of hydrogen when compared to experimental data (Bensing et al., 2022). Also important is transport (diffusive or advective) of hydrogen and/or dissolved reaction

products, as this creates concentration gradients in the pores. With the addition of temperature changes during injection/withdrawal of hydrogen, accurate and detailed investigation requires complex coupled THC models.

4. Conclusions and outlook

For continued de-risking of large-scale subsurface hydrogen storage it is crucial to comprehensively understand the potential impacts associated with hydrogen loss, contamination, and potential compromises to rock integrity related to geochemical reactions. This understanding is essential for accurately predicting hydrogen plume behaviour and ensuring recoverability. For UHS to advance beyond proof of concept, it is imperative to instil industry confidence in hydrogen reservoir safety and efficiency mitigating risks.

This review identified a consensus between many studies that hydrogen exposure under subsurface conditions, elevated pressure, and temperature can induce some abiotic mineral reactions. Most notable is pyrite to pyrrhotite conversion via dissolution-precipitation reactions, a significant reaction affecting both reservoir and caprocks. This reaction produces $H_2S_{(g)}$ as a by-product, which can reduce the quality of stored hydrogen, leading to potential corrosion to subsurface infrastructure and necessitating costly mitigation measures. This reaction is known to be catalysed by sulphate-reducing bacteria, which is commonly found in the subsurface. Additionally, hydrogen exposure can lead to carbonate (e.g., calcite) and sulphate (e.g., anhydrite) alteration. This is most prominently observed in anhydrite and calcite that are commonly found in caprock formations and can also form cements in porous rocks.

Evidence suggests limited silicate alteration due to hydrogen exposure; however, recent studies have hinted at minor reactions occurring with certain silicates under specific temperature and pressure conditions. Notably, muscovite has been observed to undergo minor but detectable changes (Yetka et al., 2018), indicating a need for further investigation to fully understand the underlying mechanisms and potential implications. These findings suggest that while the stability of silicates like quartz and feldspar remains, there is still a possibility for subtle alterations that could influence reservoir integrity. Understanding these interactions is crucial, as even minor changes can have significant implications over the long-term performance of hydrogen storage sites.

There is still uncertainty surrounding the impacts of hydrogen-induced geochemical reactions on reservoir and caprock integrity. Therefore, there is a clear need for further investigation of potential geochemical reactions under specific storage, rock/fluid chemistry, temperature, and pressures. Additionally, the interplay between abiotic and biotic reactions, particularly with microbial activity, is an identified and relevant knowledge gap, especially as it is difficult and costly to eliminate the presence of microbes in the subsurface. This will help prevent any unexpected economic or environmental impacts when field implementation begins. Overall, reservoirs primarily dominated by silicate minerals show promise for UHS, as the framework grains remain unaltered when exposed to hydrogen, preserving reservoir integrity. On the other hand, formations containing carbonate and sulphate cements, raise concerns over potential dissolution.

The pH and temperature of the system are critical parameters controlling the extent of these reactions, with pyrite reduction progressing rapidly at higher temperatures and alkalinity. Acidic reservoirs may exacerbate carbonate dissolution, necessitating pH assessments for hydrogen storage feasibility. Therefore, an assessment should be made to establish the potential reactivity of the candidate storage reservoir and the pH of the pore fluid to determine the potential for reactions between host rock and stored hydrogen. Ultimately, this review provides insights that may influence storage site selection related to geochemical reactions. Silicate-rich sandstone reservoirs and caprocks emerge as favourable options, as there is no evidence of hydrogen-induced reactions with quartz or feldspar. UHS targets may be at a lower risk of geochemical reactions between constituent minerals and hydrogen where the reservoirs contain low amounts of sulphate and carbonate minerals, as this review concludes some dissolution of these minerals may occur.

Given that hydrogen storage in porous reservoirs has never been commercially undertaken, it is imperative that laboratory experiments and field tests are conducted without any unexpected hydrogen loss or hydrogen-induced reactions. Currently, practical experience of injecting pure hydrogen into porous subsurface is limited to the depleted Rubensdorf reservoir in Austria, which began injecting in 2023 (EUH2STARS, 2024a, 2024b), and Hychico, Argentina (Pérez et al., 2016). Depleted gas reservoirs, often composed of high-purity sandstone, have additional advantages of proven security of caprocks, potential for re-using existing infrastructure to reduce capital expenses such as local transmission infrastructure and pipelines, and the presence of residual methane that could serve as a lower-cost cushion gas. However, they also have additional complications due to reactions between hydrogen and organic matter, such as residual oil, gas, and solids. It is suggested that interactions between injected hydrogen and organic matter have the potential for hydrogen trapping through adsorption on kerogen in micropores in high-organic content shales, leading to the expulsion of methane (Al-Yaseri et al., 2023b).

Overall, studies suggest that geochemical reactions are not likely to occur at an extent that will prevent the implementation of UHS in porous reservoirs. However, these studies provide guidelines for selecting reservoir and caprock formations based on mineralogical composition and reservoir conditions. Additionally, they outline some important considerations regarding processes that could impact reservoir efficiency and caprock integrity. This is important as competition for subsurface space for storage, including hydrogen, CO_2, and compressed air, is increasing as different aspects of the subsurface are explored to support low-carbon ambitions. Therefore, it is essential to match storage formations to optimise the use of the subsurface.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Lin Ma reports financial support was provided by Engineering and Physical Sciences Research Council. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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