Feasibility and prospects of symbiotic storage of \( \text{CO}_2 \) and \( \text{H}_2 \) in shale reservoirs

Lei Hou\textsuperscript{a}, Derek Elsworth\textsuperscript{b}, Jintang Wang\textsuperscript{c}, Junping Zhou\textsuperscript{d}, Fengshou Zhang\textsuperscript{e,\textasteriskcentered}

\textsuperscript{a} China-UK Low Carbon College, Shanghai Jiao Tong University, Shanghai, 201306, China
\textsuperscript{b} Energy and Mineral Engineering & Geosciences, EMS Energy Institute and G3 Center, Pennsylvania State University, University Park 16802, USA
\textsuperscript{c} School of Petroleum Engineering, China University of Petroleum (East China), Qingdao, 266580, China
\textsuperscript{d} State Key Laboratory of Coal Mine Disaster Dynamics and Control, Chongqing University, Chongqing, 400044, China
\textsuperscript{e} Department of Geotechnical Engineering, College of Civil Engineering, Tongji University, Shanghai, 200092, China

\textbf{A B S T R A C T}

Storing \( \text{CO}_2 \) and \( \text{H}_2 \) in underground repositories represents an effective approach to sequester increasing amounts of captured \( \text{CO}_2 \) for carbon neutrality and to store \( \text{H}_2 \) to promote clean energy revolutions. However, commercial/pilot-scale \( \text{CO}_2/\text{H}_2 \) storage sites are mainly restricted to conventional oil reservoirs or salt caverns – both capacity and geographic-location limited. This paper presents a systematic review of the feasibility and prospects of \( \text{CO}_2 \) and \( \text{H}_2 \) storage in fractured shale reservoirs as secure repositories. Both field pilot and laboratory studies of \( \text{CO}_2 \) injection in shales are cross-analyzed across various spatial and time scales, to provide a reliable and substantial basis to support new findings. The presence of suitable injectivity and adequate sealing capacity in shale are demonstrated. The fracture networks are shown to provide major storage space in shales, contrasting with the pore system in conventional reservoirs. This difference in storage mechanisms results in an overestimation in the storage capacity of shales when applying porous-medium-based methods. An underestimation in the mass of injection, however, is apparent from a single well for the reported cases due to unknown characteristics of underground fracture networks. The symbiotic storage of \( \text{CO}_2 \) and \( \text{H}_2 \) in shale is discussed in its feasibility and ability to improve both \( \text{CO}_2 \) storage but principally \( \text{H}_2 \) recovery – due to the presence of a gas cushion. A new equivalent-fracturing method is proposed as a supplement to recalibrate the over- and underestimated prospects of \( \text{CO}_2/\text{H}_2 \) storage in shales – a necessary component in reducing carbon emissions and accelerating the energy transition.

1. Introduction

Geological storage of \( \text{CO}_2 \) and \( \text{H}_2 \) are essential components in mitigating global warming and enabling the energy transition [1–4]. In 2021, global energy-related \( \text{CO}_2 \) emissions remained at 33.0 Gigatonne (Gt) [5]. For economic reasons, a survey by the Global CCS (Carbon Capture and Storage) Institute shows that almost 80% of commercial CCS projects – 24 out of 31 as of 2022, are performed in oil reservoirs for EOR (Enhance Oil Recovery) [6]. \( \text{CO}_2 \) improves the mobility of crude oil by reducing oil viscosity, which stimulates the production and sequestration of \( \text{CO}_2 \) by replacing in-situ oil [7–9]. However, assuming that all the produced oil is replaced by \( \text{CO}_2 \), the global \( \text{CO}_2 \) storage (4.2 Gt in 2021, ignoring the density difference between \( \text{CO}_2 \) and oil) is still far below (~13%) the required annual storage demand (33.0 Gt) [10].

Meanwhile, a different situation but maybe the same solution exists in the development of geological storage for \( \text{H}_2 \) [11,12]. Initially tested in salt caverns, more exploration in a broader suite of potential repository geological environments is critical for \( \text{H}_2 \) storage to improve volume capacity and stability [13–16], promote investment for construction [17–21], and bridge the disparate spatial range of storage sites and scattered market distribution [4,22,23]. Therefore, the available capacity of repositories requires an expansion of geological storage for both \( \text{CO}_2 \) and \( \text{H}_2 \), in order to meet the increasing demand for carbon neutrality and promote the clean energy transition.

Shale reservoirs can be optimized for storing \( \text{CO}_2 \) and \( \text{H}_2 \). Prospective resources in shale comprise an estimated 7576.6 trillion cubic feet of gas and 418.9 billion barrels of oil – far in excess of current worldwide reserves (293 billion barrels) as assessed by the Energy Information Administration (EIA) [24,25]. Interestingly, China and the U.S., heading...
the CO₂ mission country list, also lead in the development of, and production from, shale reservoirs [5,26]. Large reserves with broad geographic distribution and active investment potentially favor CO₂ and H₂ storage in shale [27–30]. Moreover, the extremely low permeability of the shale matrix in naturally fractured reservoirs enhances the intrinsic safety of CO₂ and H₂ storage by constraining migration [31–34]. Used as a working fluid, CO₂ can improve the efficiency of oil/gas recovery in shale by creating and accessing more complex fracture networks [35–38], replacing CH₄ with its higher adsorption capacity [39–42] and reducing oil viscosity for miscible displacement [43–46].

Mechanisms of fluid storage (in-situ oil/gas and injected CO₂/H₂) in shale are different from those in conventional porous reservoirs [47]. Conventional reservoirs for oil and gas usually comprise a connected pore system within highly permeable rocks (milidarcy level) that are sealed by an impermeable caprock to provide structural (anticline and fault) and/or stratigraphic (facies change) traps [48–50]. Thus, conventional reservoirs store CO₂ and H₂ in the same way as trapping oil and gas [51–53]. However, shale reservoirs contain oil and gas as a result of their nano-darcy-level permeability – maybe six orders of magnitude lower than the permeability of conventional reservoirs [54–56]. Shale reservoirs have to be artificially fractured by massive hydraulic fracturing to create conductive fracture networks before production may begin [57–59]. This artificial intervention generates a fracture-pore system for oil and gas production that is then available for enhanced oil/gas recovery (EOR/EGR) and which is significantly more complex than the connected pore system in conventional reservoirs [60–63]. The adsorption, dissolution and diffusion behaviors of CO₂ in shale fractures and matrix represent the basic mechanisms for its permanent storage. Although a few field pilots for CO₂ storage in shale have been conducted, a significant gap still exists between lessons learned from field pilots and laboratory studies [64–68] – for instance, the limited injection scales in situ and the enormous estimated storage capacity. Currently, the idea of storing H₂ in shale is more conceptual. Research work mainly assesses sealing performance in shale and the periodic injection-recovery performance [69], which is one of the major differences compared with the permanent storage of CO₂. Therefore, technical innovations and more targeted research are needed to advance the commercialization of CO₂ and H₂ storage in shale reservoirs.

This paper provides a comprehensive review and analysis of CO₂ and H₂ injection in shale. First, field-scale pilots of CO₂ injection in shales are summarized. Their feasibility is demonstrated by confirming the injectivity of CO₂ in fractured and intact shales and by noting the sealing performance of the shale matrix. Second, a critical review of relevant literature, focusing on the outcomes and lessons-learned from field pilots, is summarized to delineate principle mechanisms of CO₂/H₂ injection and storage. Then, analyses synthesizing field tests and laboratory studies are conducted and reported to generate critical perspectives. Recommendations for CO₂ and H₂ storage in shale reservoirs are proposed to improve both the estimation of storage capacity and the efficiency of field pilots – a credible technology pathway to carbon neutrality and new energy transition.

2. Field pilots – feasibility and observations

Field demonstration projects play a crucial role in the development of rational methods for subsurface storage by surmounting the intrinsic scale limitation of laboratory research [70–72]. Typical cases of CO₂ injection in unconventional shale formations are summarized and analyzed to validate the feasibility of the approach and summarize important observations. As an adjunct, geological storage of H₂ in shale is currently conceptual [73–75], but may be advanced through documenting experiences of CO₂ injection because of the similarity of the anticipated injection process and anticipated reservoir conditions.

2.1. Field records of CO₂ and H₂ storage

Injecting CO₂ into oil and gas reservoirs to improve production can be traced back to the 1980s inclusive of the use of CO₂ foams, energized fracturing fluids and other approaches [76–78]. Representative cases are summarized in chronological order in Table 1 by restricting the consideration to shale reservoirs and pure-CO₂ injection. Cases 1–4 are early attempts in Bakken and Chattanooga shales in North America since 2008 [79]. Cases 5–7 are recent pilot studies in China using CO₂ as hybrid fracturing fluids (Table 1). All cases are operated by energy companies with the desire to develop a generic and improved stimulation technique. CO₂ is injected into both artificially-fractured and initial-intact shale reservoirs for enhanced oil/gas recovery (EOR/EGR) and permanent sequestration of CO₂. The phase of the CO₂ is initially liquid and is transformed into either gaseous or supercritical states depending on the pressure and temperature of reservoirs [80–84]. The scale of these injections varies between ~100 and 3000 tons for a single well. The injection rate is typically measured in days for huff and puff injections (Cases 1–3, Table 1) and in minutes for hydraulic fracturing injections (Cases 5–7, Table 1). Correspondingly, the wellhead pressure is much lower in the huff and puff cases (~3.45 MPa) than for hydraulic fracturing (~60 MPa). This paper focuses on storing CO₂ in shale when analyzing field tests and fundamental research, for instance, in examining injectivity, sealing performance and migration, among other parameters. The aspects of enhanced oil and gas recovery by CO₂ are not the focus of this study.

The concept of H₂ storage is discussed together with that of CO₂ storage since the case for H₂ storage in shale is rarely reported. The geological storage of H₂ is mainly restricted within salt caverns, as shown in Table 2. Noteworthy, is that CO₂ is a common impurity during hydrogen production, for instance, grey hydrogen (H₂) obtained from the gasification of coal. Low-purity H₂ mixed with CH₄, N₂, CO and CO₂, is used as town gas in European projects (Germany, France and Czech Republic), as presented in Table 2. Although CO₂ is not injected by design in H₂ storage sites, the geological coexistence of CO₂ and H₂ is feasible based on field pilots. Further laboratory studies show that the injection of CO₂ as a cushion gas can boost reservoir pressure, prevent water breakthrough, and then enhance the recovery and purity of H₂ production in salt caverns and aquifers [53,73,75]. Moreover, our previous studies indicate that the adsorption of CO₂ onto organics and clays swells the shale matrix and potentially reduces fracture permeability – sometimes significantly [40,85,86]. Therefore, high contents of organics and clays in shales (a unique feature compared with salt caverns or
Table 1
Summary of CO₂ injection cases in shale reservoirs [64–68].

<table>
<thead>
<tr>
<th>No.</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
<th>Case 5</th>
<th>Case 6</th>
<th>Case 7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Year</td>
<td>2008</td>
<td>2009</td>
<td>2014</td>
<td>2017</td>
<td>2017</td>
<td>2018</td>
<td>2019</td>
</tr>
<tr>
<td>Well No.</td>
<td>NDIC 16713</td>
<td>Burning Tree-</td>
<td>Hw-1003</td>
<td>Knutson-Werre</td>
<td>Yan-2011</td>
<td>BYY-1HF</td>
<td>Jiye-1HF</td>
</tr>
<tr>
<td>Operator</td>
<td>EOG Resources, Inc.</td>
<td>Continental</td>
<td>VCCER/Cardno Ltd/</td>
<td>EERC/XTO Energy</td>
<td>Yanchang Oil</td>
<td>SINOPEC</td>
<td>PetroChina</td>
</tr>
<tr>
<td>Location</td>
<td>Parshall Field, North Dakota</td>
<td>Elm Coulee Field, Montana</td>
<td>Boone Camp Field, Tennessee</td>
<td>Dunn County, North Dakota</td>
<td>Ordos Basin, Shaanxi</td>
<td>Jianghan Oilfield, Hubei</td>
<td>Jilin Oilfield, Jilin</td>
</tr>
<tr>
<td>Formation</td>
<td>Upper Bakken Shale</td>
<td>Middle Bakken Shale</td>
<td>Chattanooga Shale</td>
<td>Middle Bakken Shale</td>
<td>Yanchang Formation</td>
<td>Formation Inter-shale Sealing</td>
<td>Formation Shale</td>
</tr>
<tr>
<td>Depth</td>
<td>–</td>
<td>–</td>
<td>–1120 m</td>
<td>–3377 m (MD²)</td>
<td>–2940 m</td>
<td>–3358 m</td>
<td>2420–2500 m</td>
</tr>
<tr>
<td>In-situ Fluid</td>
<td>Oil</td>
<td>Oil</td>
<td>Gas</td>
<td>Oil</td>
<td>Gas</td>
<td>Oil</td>
<td>Oil</td>
</tr>
<tr>
<td>Reservoir Integrity</td>
<td>Fractured</td>
<td>Fractured</td>
<td>Intact</td>
<td>Intact</td>
<td>Intact</td>
<td>Intact</td>
<td>Intact</td>
</tr>
<tr>
<td>Well Completion</td>
<td>Horizontal/6 stages</td>
<td>Horizontal/4 stages</td>
<td>Vertical well</td>
<td>Vertical well</td>
<td>Horizontal/5 stages</td>
<td>Horizontal/18 stages</td>
<td></td>
</tr>
<tr>
<td>CO₂ Injection Scale</td>
<td>1325 tons</td>
<td>2570 tons</td>
<td>510 tons</td>
<td>99 tons</td>
<td>386 m³</td>
<td>1564 m³</td>
<td>3265 m³</td>
</tr>
<tr>
<td>Fluid Component</td>
<td>Pure CO₂</td>
<td>Pure CO₂</td>
<td>Pure CO₂</td>
<td>Pure CO₂</td>
<td>Pure CO₂ &amp; gel</td>
<td>Pure CO₂ &amp; gel</td>
<td>Pure CO₂ &amp; gel</td>
</tr>
<tr>
<td>Injecting Rate</td>
<td>–</td>
<td>–</td>
<td>40.95 tons/day</td>
<td>25 tons/day</td>
<td>–2 m³/min²</td>
<td>–2 m³/min²</td>
<td>–4 m³/min²</td>
</tr>
<tr>
<td>Wellhead</td>
<td>–</td>
<td>–</td>
<td>–3.45 MPa</td>
<td>–28.8 MPa³</td>
<td>–20 MPa</td>
<td>–60 MPa</td>
<td>–52 MPa</td>
</tr>
<tr>
<td>Sealing behavior/CO₂ Breakthrough</td>
<td>One far offset well is affected, but three nearby wells are not.</td>
<td>No offset-producing wells are affected.</td>
<td>No tracer (SF₆ and PFTs) is detected from any offset well.</td>
<td>The injectivity of the Bakken shale is relatively low.</td>
<td>–</td>
<td>Micro-seismic events are observed during CO₂ injection.</td>
<td>Micro-seismic events are observed during CO₂ injection.</td>
</tr>
<tr>
<td>Other Observations</td>
<td>Local natural fracture system may dominate the breakthrough.</td>
<td>–</td>
<td>CO₂ exists as gaseous in the reservoir.</td>
<td>Production of light-oil increases. No fracture is generated.</td>
<td>–</td>
<td>Production of light-oil increases.</td>
<td>Less volume of CO₂ is needed to generate a micro-seismic event.</td>
</tr>
</tbody>
</table>

² MD – measured depth, is the length of the wellbore, and is greater than the vertical depth.
³ The unit represents the injected volume of liquid CO₂ per minute.

Table 2
Sites for geological storage of hydrogen. Adapted with permission from Ref. [52], copyright (2021) Elsevier.

<table>
<thead>
<tr>
<th>Field/Project Name</th>
<th>Reservoir</th>
<th>H₂/ %</th>
<th>Impurities</th>
<th>Working Pressure/MPa</th>
<th>Depth/ m</th>
<th>Volume/ m³</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teeside (UK)</td>
<td>Bedded salt</td>
<td>95</td>
<td>–4% CO₂</td>
<td>4.5</td>
<td>365</td>
<td>210,000</td>
<td>Operating</td>
</tr>
<tr>
<td>Clements (US)</td>
<td>Salt cavern</td>
<td>95</td>
<td>–</td>
<td>7.0–13.7</td>
<td>1000</td>
<td>580,000</td>
<td>Operating</td>
</tr>
<tr>
<td>Moss Bluff (US)</td>
<td>Salt cavern</td>
<td>95</td>
<td>–</td>
<td>5.5–15.2</td>
<td>1200</td>
<td>566,000</td>
<td>Operating</td>
</tr>
<tr>
<td>Spindletop (US)</td>
<td>Salt cavern</td>
<td>95</td>
<td>–</td>
<td>6.8–20.2</td>
<td>1340</td>
<td>906,000</td>
<td>Operating</td>
</tr>
<tr>
<td>Kiel (Germany)</td>
<td>Salt cavern</td>
<td>60</td>
<td>–30% of N₂, 10–33% of CH₄ and 12–20% of CO and CO₂</td>
<td>8.0–10.0</td>
<td>–</td>
<td>200–250</td>
<td>Operating</td>
</tr>
<tr>
<td>Kotzin (Germany)</td>
<td>Aquifer</td>
<td>62</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>32,000</td>
<td>Closed</td>
</tr>
<tr>
<td>Beynes (France)</td>
<td>Aquifer</td>
<td>50</td>
<td>–</td>
<td>9.0</td>
<td>430</td>
<td>3.3 × 10⁶</td>
<td>Operating</td>
</tr>
<tr>
<td>Lobodice (Czech Republic)</td>
<td>Aquifer</td>
<td>50</td>
<td>–</td>
<td>1.0</td>
<td>600</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Diadema (Argentina)</td>
<td>Depleted Gas</td>
<td>10</td>
<td>–</td>
<td>7.8</td>
<td>1000</td>
<td>–</td>
<td>Operating</td>
</tr>
</tbody>
</table>

aquifers) may enhance the cushion-gas function of CO₂ to restrain H₂ leakage and boost the recovery rate – this observation inspires a potential strategy for the symbiotic storage of CO₂ and H₂ in shales.

2.2. Injectivity of CO₂ in fractured and intact shales

The feasibility of injectivity of CO₂ is a prior concern for shale reservoirs because of their initial nano-scale permeability [87,88], which elevates injection pressures and then influences the efficiency (operation period) and economics (usage of pumps and wellhead) of CO₂ storage. For artificially fractured reservoirs, 128–2570 tons of CO₂ can be injected for one stage of a horizontal well (Cases 1–3). This number is approximately 199–344 tons/stage for an unfractured shale reservoir (Cases 6 and 7) [66,68]. Even at the smallest scale (510 tons in total), the

a. The units of field measurements are unified for comparison.

b. This pressure is converted from the bottom hole pressure (9500 psi) based on the MD (3337 m) and the density of liquid CO₂ (1100 kg/m³), thus lower than the actual wellhead pressure.

c. More details of the observations are explained in Sections 2.2 and 2.3.
amount of injected CO$_2$ for Case 3 is close to the historical hydraulic fracturing scale (amount of previously injected fluid) [64]. The hydraulic injection history for Case 3 is presented in Fig. 1. The average injection rate is ~40 tons/day, which is lower than typical fracturing operations (Cases 5–7) but higher than injection tests in unfractured shale (Case 4) [65]. The wellhead pressure increases slowly and remains lower than 500 psi (3.45 MPa). CO$_2$ may be injected into existing fractures considering the high pressure for CO$_2$ to penetrate or fracture the intact shale matrix in Cases 4–7.

Injection of CO$_2$ in an intact shale reservoir requires greater hydraulic power, resulting in higher wellhead pressures, as shown in Fig. 1. In Case 4, downhole gauges are applied to measure the reservoir pressure and temperature during the test. The pressure in Case 4 represents the bottom-hole pressure and is slightly higher than the pore pressure (8668 psi), which is insufficient to induce fracture. The pressure differential, however, drives CO$_2$ to slowly penetrate the shale matrix in the days following injection – as evident in the diminishing wellbore pressure with time post-injection (after 15 h) in Fig. 1. The injection rate jumps between 6 and 12 gpm (0.0225–0.045 m$^3$/min), which is much lower than the pump rates applied in fracturing operations (Cases 5–7). However, the wellhead pressure (converted from downhole pressure based on well depth and density of liquid CO$_2$) approaches 28.8 MPa, indicating the difficulty in CO$_2$ injection into the intact shale matrix. Therefore, artificial fracture networks significantly improve the injectivity of CO$_2$, as evident in comparing injection pressures between Cases 3 and 4 (as shown in Fig. 1).

2.3. Sealing performance of shale

The sealing efficiency of fractured shale is another essential issue in the geological storage of CO$_2$ [89–91]. Pressure and production monitoring are performed in neighboring wells adjacent to the injecting well in Cases 1–3. Only one offset well one mile away from the injection well in Case 1 detects the CO$_2$ breakthrough during the injection, which may result from transmission through existing fractures [79]. However, three nearby wells within one-mile separation from the injection are not affected in Case 1. Suggesting that the characteristics of the local natural fracture system control this response. Neither abnormal pressure (pressure variations induced by CO$_2$ breakthrough) nor variation in production is reported in neighboring wells near injection in Cases 2 and 3. Hexafluoride (SF$_6$) and two perfluorocarbon tracers (PFTs) are injected with the CO$_2$ in Case 3, but no tracers are detected in offset wells during the injection and soaking period (4 months), indicating the sealing performance of depleted shale reservoirs [92,93].

2.4. Fracturing efficiency and recovery of injected CO$_2$

Injecting pure CO$_2$ can generate fractures in shale by elevating the hydraulic injection power [86,94–96]. Micro-seismic interpretation in Cases 6 and 7 suggests massive rock failure events during the pre-injection of CO$_2$, as shown in Fig. 2 [66]. This case uses a hybrid fracturing method, where pure CO$_2$ and water-based fluid are injected successively (Fig. 2 a) [97]. The declining pressure under a constant injection rate before 60 min (highlighted by the yellow rectangle) in Fig. 2 (a) also indicates the creation and propagation of fractures [98,99]. The statistics show that injection of every 6.5 m$^3$ of CO$_2$ and 30 m$^3$ of gel generates a single micro-seismic event, which is ~5 times more efficient in comparing CO$_2$ against water-based fluids [66]. The higher fracturing efficiency of CO$_2$ (lower volume of injected fluid to generate a microseismic event) may be due to its lower viscosity and higher diffusivity in its natural supercritical state under reservoir conditions [100–102]. Noteworthy is that the fracture length created by CO$_2$ fracturing is comparable with the length fractured by the following hydraulic injection, as presented in the plan views in Fig. 2 (b).

Quantifying the mass recovery of injected CO$_2$ is critical in terms of CO$_2$ storage in oil and gas reservoirs because CO$_2$-EOR does not necessarily favor the permanent storage of CO$_2$ [103–106]. CO$_2$ will preferentially dissolve and mix in the native reservoir-oil, and then increase production of light oil (as presented in Cases 4 and 6) – one of the core mechanisms of the CO$_2$-EOR technique [107–109]. Approximately 50 % of the injected CO$_2$ (1285 tons) is reproduced along with the oil in three months, as presented in Case 2 (Table 1). The recovery of CO$_2$ from shale gas formations is moderate – ~41 % of the injected CO$_2$ in 17 months, as shown in Fig. 3 (a). The interaction between CO$_2$ and the shale matrix

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**Fig. 1.** The hydraulic measurements of CO$_2$ injection for (a) Case 3 (fractured shale reservoir) [64] and (b) Case 4 (intact shale reservoir) [65]. Redrawn with permission from Ref. [64], copyright (2017) Elsevier. (This figure has been completely redesigned and redrawn by the authors of the present manuscript).
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Fig. 2. Field measurements for Case 7. (a) Injection records of the 10th Stage; (b) Micro-seismic interpretations for the 14th Stage [66].

Fig. 3. Recovery of CO2 after injections in (a) Case 3 (CO2 huff-and-puff) [64] and (b) Case 5 (CO2 fracturing) [67]. Redrawn with permission from Ref. [64], copyright (2017) Elsevier. (This figure has been completely redesigned and redrawn by the authors of the present manuscript).

may trap, then obstruct the flowback of CO2, for instance, the adsorption of CO2 onto organics and clays and their swelling effects, the dissolution of CO2 and diagenetic reactions, among other processes [110–115]. Therefore, dry gas shale formations may be preferable for CO2 storage compared to oil shales. Moreover, injecting CO2 as a fracturing fluid may boost the CO2 trap in shale. The higher injecting pressures drive CO2 more deeply into the shale matrix from the bounding fractures. Proppant-inaccessible fractures (microfractures that allow access only for CO2) close after fracturing injection, which will seal CO2 in disconnected fractures. These mechanisms act against CO2 recovery in the cases of CO2 fracturing (~2% of CO2 in Case 5), compared with the CO2 concentrations for huff-and-puff injection (~10% of CO2 in Case 3) as shown in Fig. 3.
3. Laboratory studies regarding field observations

Fundamental studies related to field tests are surveyed to define field-scale mechanisms of flow and storage, define a necessary research focus and reveal gaps between research and application. A systematic analysis is performed from the perspective of CO$_2$ and H$_2$ storage in shale, relating to storage capacity, recovery of the injected CO$_2$, and the feasibility of H$_2$ storage.

3.1. Estimation of CO$_2$ storage in shale

Methods of evaluation of the storage potential in conventional reservoirs are usually employed for unconventional reservoirs, which report the enormous potential of CO$_2$ storage in shales [34, 116]. The CO$_2$ storage capacity in shale can be assessed either on a volumetric basis [31, 117] or on a production-based basis [118]. The representative volumetric method is proposed by the United States Department of Energy National Energy Technology Laboratory (U.S. DOE NETL) [119]. The volumetric equation considers the effective reservoir area, thickness, pore volume, CO$_2$-sorbed volume, and gas-rock contact area. This method provides a theoretical storage capacity of CO$_2$ assuming 100% of the in-situ fluids are replaced by injected CO$_2$ [120, 121]. The production-based method is based on the same constraints of CH$_4$ flow out-from and CO$_2$ transport back-into the same formation. Models for CH$_4$/CO$_2$ sorption equilibria and kinetics are utilized together with published CH$_4$ production data for evaluation [118]. The volumetric approach has been previously used to estimate the CO$_2$ storage capacity in the Ohio and New Albany shales (~28 Gt) [122], and in the Marcellus shale (~171 Gt) [31]. Using the production-based approach, a time-dependent curve of CO$_2$ storage suggests that ~18.4 Gt of CO$_2$ can be stored in Marcellus Shale by 2030, as shown in Fig. 4 [118]. Moreover, numerical models of shale reservoirs simulate the process of CO$_2$ injection and evaluate the efficiency of CO$_2$ storage. Different injecting models (CO$_2$ flooding and huff-and-puff) are tested based on mechanisms of adsorption, dissolution, diffusion, and compaction. CO$_2$ flooding and huff-and-puff improve gas production by 24% and 6%, respectively, based on data from the Barnett shale, which agrees with field observations (~15%) in Case 3 (Table 1). The injected CO$_2$ is stored in free, adsorbed and dissolved states in the proportions of 42%, 55%, and 3%, respectively [122]. Moreover, CO$_2$ storage capacity is found to have a time dependency over the lifetime of a CO$_2$ storage project [124]. Research suggests that CO$_2$ is mainly trapped in a free state over the short term (i.e. decades), then is mineralized significantly over the long term (thousands of years) in Yanchang shale, as shown in Fig. 5 [125]. Estimation of CO$_2$ storage in Devonian shale shows that porosity and adsorption, respectively, contribute 50% of the storage capacity [126].

3.2. Efficiency of CO$_2$ storage – recovery issue

The co-recovery of CO$_2$ together with oil and gas is a severe issue in a producing reservoir (Cases 2 and 3, Table 1), which may determine the efficiency of permanent CO$_2$ sequestration. However, injecting CO$_2$ to enhance oil and gas recovery (EOR/EGR) is currently the most economic and frequent way to perform CO$_2$ storage in reservoirs [127–130]. Numerical simulations, combining micro-seismically-interpreted fracture networks, predict a CO$_2$ storage efficiency (ratio of sequestered and injected CO$_2$) as low as 21.3% after 20 years for one cycle of huff-and-puff injection in Longmaxi shale, in China [131]. The efficiency of CO$_2$ storage may be improved by performing continuous injection-production cycles, annually. Starting from ~20%, the efficiency increases continuously and approaches ~90% by 30 years in both Bakken oil shale (Fig. 6 a) and the Eagle Ford gas shale (Fig. 6 b) [122]. The average efficiency of CO$_2$ storage varies between 30% and 80% depending on the specific reservoir and injection schedule. The selection of injection pressure is observed to dominate the efficiency among the engineering and geological factors (injection rate, injection time, number of cycles, carbon dioxide soaking time, fracture half-length, fracture conductivity, fracture spacing, porosity, permeability, and initial reservoir pressure), as shown in Fig. 6.

3.3. Feasibility of H$_2$ storage in shale

Candidates for the geological storage of H$_2$ (including salt and rock caverns, saline aquifers, and depleted oil and gas reservoirs) are analyzed from the perspectives of capacity, stability, cost and transport to highlight the feasibility of H$_2$ storage in shales [133–135]. As a valuable fuel, pilot tests of H$_2$ storage are mainly performed in salt caverns to control the dissipation and purity (Table 2). However, unique advantages and perspectives of H$_2$ storage in shale are apparent in the aspects of capacity, stability, cost and transport. For inter-seasonal storage and adjustment, porous depleted reservoirs can offer capacities several orders of magnitude larger than salt caverns [52, 69, 74]. This storage capacity is also more stable in rock-based reservoirs than the capacity in salt caverns that are subject to deformation and fatigue damage and failure of salt under cyclic loading [136–138]. The costs of geological H$_2$ storage in different underground storage sites may be analyzed and compared. The most economical candidate is depleted reservoirs at 1.23 USD/kg of stored H$_2$ followed by aquifers at 1.29 USD/kg, then caverns at 1.61–2.77 USD/kg for salt and hard rock caverns [139]. Among depleted reservoirs, the construction and operation costs are lower for depleted gas reservoirs than the costs for depleted oil reservoirs [23]. Moreover, oil and gas reservoirs are more widely and ubiquitously distributed than the limited geological location-specific salt cavern sites that are potentially far from markets. Recycling pre-existing oil and gas infrastructure for H$_2$ production and transport can furthermore save on the necessarily large capital investment. A comprehensive benchmarking result of different underground options is presented in Fig. 7, suggesting that salt caverns, depleted gas reservoirs and aquifers (ranking from the first to the third) are preferential considering safety, feasibility, cost and operation [140].

H$_2$ storage in gas shale reservoirs is investigated via reservoir simulations (as shown in Fig. 7) to reveal the contributions of matrix permeability, injection scale, and period length of the injection cycle on the recovery and purity of H$_2$. The simulation results, focusing on Haynesville shale, indicate that H$_2$ recovery increases from 35.2% for a short-term (12 h) cycle to 68.7% for an intermediate-term (30 days) cycle, both for large-scale (thousands of tons of H$_2$) injections [69]. For small-scale (hundreds of tons of H$_2$) injections, the recovery efficiency increases from 44.7% for a short-term cycle to 71% for a long-term (120 years) cycle (thousands of years) in Yanchang shale, as shown in Fig. 5 [125].
days) cycle, which is mainly dominated by the well shut-in and pressure build-up due to the remaining methane [69]. Without aid from a gas cushion (for instance, CO₂, CH₄, or other gases), this recovery is comparable to the estimated recovery of H₂ from conventional reservoirs (50 %~ 87 %) [74] and saline aquifers (~78 %) [141]. The tightness of the shale matrix remains essentially impermeable to H₂ (H₂ penetrates only marginally into the matrix) when the matrix permeability is lower than 0.001mD [69]. Hydrogen is, therefore, mainly stored within hydraulic fractures. Moreover, shale gas reservoirs are usually dry when devoid of water production, which mitigates the H₂-hysteresis mechanisms, such as relative permeability [142], capillary pressure [93], interfacial tension [143–145], and contact angles [146].

4. Cross-validation and critical reviews

Observations of field tests and laboratory studies are summarized and cross-analyzed for critical perspectives and definitions of new mechanisms and methods, as shown in Fig. 8. Field pilots have demonstrated the feasibility (injectivity and sealing performance) of CO₂ storage in shales. Laboratory studies reveal the mechanisms and extrapolate the time scales of CO₂ injection. This comprehensive analysis of field and laboratory evaluations provides an integrated review of mechanisms and outcomes.

4.1. Overestimation of CO₂ storage capacity in shale

Porous-medium-based methods applied to conventional reservoirs are often inappropriately employed in assessing the storage capacity in unconventional shales (fracture-dominant) – potentially resulting in overestimation, as illustrated in Fig. 9. Both volumetric and production-based methods evaluate CO₂ storage capacity based on the “dual porosity – with fractures for flow and matrix for storage” feature of shales [117,119,122]. The fractures (natural and artificial fracture networks) in shale provide a high-conductivity flow path for the initial high rate of production of oil or gas [57,147]. However, production rates soon drop dramatically as fractures are drained, followed by a slow fall-off of production as oil/gas migrates from the matrix to fractures [148–150]. Current evaluation methods assume that the injected CO₂ would follow the reverse path – quickly filling the fracture networks and then penetrating into the matrix [118,119]. This assumption is tenable for conventional reservoirs with high permeability (milidarcy level) and connected-macro/micropore systems in the rock matrix (Fig. 9 a), but may fail for extremely-tight shales with nano-darcy-level permeabilities and more isolated pores in the matrix (Fig. 9 b) [151,152]. The volumetric method presumes that all in-situ fluids in the pores are replaced by CO₂, which may ignore the prerequisite of having a connected fracture network – providing a flow path [153]. Although the volumetric reach of horizontal wells and hydraulic fracturing create penetrative fracture networks, the volume of this fracture-accessible space is still small in comparison with the basin-scale reservoir volumes representing the storage capacity [58] – even taking all wells and their stimulated volumes into account. This gap results in an overestimation of CO₂ storage capacity in shale when using the volumetric evaluation method. Moreover, the recovery issue decreases the storage efficiency, which is also crucial in this overestimation.

Even with sufficiently penetrative and connected fracture networks, the penetration of CO₂ into the shale matrix will consume a significant amount of energy and evolve over an extended time, as tested in Case 4 (Fig. 1). The matrix-fracture-well flow path for oil and gas may be reversed in conventional reservoirs, which is the principal mechanism for flooding – injecting CO₂ from one well and producing oil/gas from an offset well through the matrix [154,155]. This flooding technique, however, is rarely applied to shale reservoirs because of their impermeable matrix that obstructs production in offset wells, as the monitoring observations in Cases 1–3 (Table 1). Studies also show that if a conventional reservoir can accept one standard cubic meter of CO₂ per second per square meter of the exposed wellbore, then the shale reservoir would require a million seconds (11.6 days) to accept the same amount of CO₂ under those same conditions – that is 1 s versus one million seconds [119]. Therefore, the penetration of CO₂ into a shale matrix relies on the driving energy (pressure) and time, which is also demonstrated by the high wellhead pressures apparent in Cases 4–7 (Table 1) and in the dominant influence of injection pressure in the efficiency of CO₂ storage (Fig. 6). This mechanism is neglected when deriving the production-based evaluation method, thus resulting in the overestimation [118]. The production of hydrocarbons is driven by sustaining continuous geological stress and in-situ pore pressure, while the artificial injection of CO₂ is limited by the capacities of wellhead equipment and pumps, the economic efficiency and injecting time. Consequently, storing CO₂ in fracture networks in shales may be more feasible and efficient than in the matrix, which is also observed in the numerical simulation of H₂ storage in shale [69].

4.2. Underestimation of CO₂ injection in single well

The scale of injected CO₂ in fractured reservoirs varies between 128 tons/stage and 2570 tons/stage as presented in Table 1 (Cases 1–3). Case 3, at the smallest injection scale, is designed based on the fracturing
scale, namely, the volume of injected CO$_2$ is approximately equal to the volume of injected fluids for the prior fracturing [64]. According to this principle, a typical stage for shale gas fracturing in the Sichuan Basin (China) consumes ~2000 m$^3$ of liquid [156,157], which may be equivalent to a CO$_2$ storage capacity exceeding 2000 tons/stage. Similarly, the scales of CO$_2$ injection in Cases 6 and 7 may achieve only ~19.7 % (1564 m$^3$ of CO$_2$; 7944 m$^3$ of total fluids) and ~9.4 % (3265 m$^3$ of CO$_2$; 34,808 m$^3$ of total fluids) of the capacity, respectively, and thus are underestimated. This can be further demonstrated by the low and high injecting pressures in Cases 3 and 4, respectively. The injection of CO$_2$ may mainly fill the fracture networks and replenish the formation pressure. If the injection scale had exceeded the maximum capacity of the fractures, CO$_2$ would either reactivate fractures or penetrate into the shale matrix by respectively overcoming the minimum horizontal stress and the in-situ pore pressure [158,159]. Correspondingly, the wellhead pressure should be $>3.45$ MPa referring to the pressure in Case 4 (~28.8 MPa, Table 1).

This underestimation may result from the unknown characteristics of the fracture networks, the physical characteristics of CO$_2$ as a supercritical fluid and uncertainties in the pressures and fluids in the shale.

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Fig. 6. Retention percentage (ratio of CO$_2$ remaining in the subsurface to the total injected CO$_2$) with respect to “Year” and “Injection Pressure” for CO$_2$ Huff-and-Puff injection in (a) the Bakken oil shale and (b) the Eagle Ford gas shale. Redrawn with permission from Ref. [132], copyright (2018) Elsevier.
The precise detection of underground fractures (several millimeters wide) in reservoirs is technically infeasible when thousands of meters away from the surface [160]. Expensive micro-seismic monitoring can only estimate the stimulated reservoir volume [161]. Thus, the complexity of fracture networks in shale exacerbates the difficulties in its characterization. Meanwhile, the high diffusivity and fully miscible and absence of a capillary exclusion pressure apparent for supercritical CO$_2$ enable it to access smaller fractures than does water, more
completely connect the fracture network and thus activate a more voluminous space for storage [40]. The dissolution and adsorption of CO$_2$ in local groundwater, organics and clay also consume a certain amount of CO$_2$, as shown in Fig. 5 (a). Moreover, the historic production of the reservoir generates a pressure drawdown distribution around the well and fractures [162, 163]. Injected CO$_2$ may be preferential to replenish the deficit of pressure in the matrix due to the larger pressure difference. Therefore, increasing the injection scale and wellhead pressure may be necessary to improve the efficiency of CO$_2$ storage in a single well [86]. The elevation of wellbore pressures, however, should be performed gradually and with care for leakage, since CO$_2$ fracturing can generate long fractures as reported previously (Case 7, Fig. 2 b).

### 4.3. Feasibility of symbiotic storage of CO$_2$ and H$_2$ in shale

Using CO$_2$ as a cushion gas for H$_2$ storage may improve both the permanent sequestration of CO$_2$ and the periodic injection-recovery of H$_2$, as presented in Fig. 10. The existence of H$_2$ in shale reservoirs provides a persistent pressure to drive more CO$_2$ deeper into the shale matrix, which promotes permanent storage of CO$_2$. The prior injected CO$_2$ may swell the shale matrix by the adsorption effects and then compact fractures to enhance the sealing performance for H$_2$ storage [40, 85, 86]. The stored CO$_2$ and native and remaining CH$_4$ in the reservoir are optimized cushion gases (these could be ~150 % of the stored H$_2$) to replenish the deficit of reservoir pressure, which is essential to enhance recovery of H$_2$ [73, 164]. A depleted dry gas reservoir could be an option for this integrated CO$_2$ and H$_2$ storage scheme, which would take advantage of the seal performance in shale reservoirs and avoid the intrinsic problems in using conventional oil reservoirs (dissolution of H$_2$ and water breakthrough, among others) [165]. This new strategy requires a comprehensive triple-component simulation involving CH$_4$ production, CO$_2$ sequestration, and H$_2$ injection and production [53, 73, 75, 166], as well as research on the chemical and microbial reactions of H$_2$ in shale. Moreover, CO$_2$ is expected to be permanently sequestrated in shale reservoirs, whilst H$_2$ will be cyclicly injected then recovered, repetitively. Further mechanistic studies (for instance, defining CO$_2$–H$_2$ multiphase flow in shale fractures) are essential to optimize the scheduling and cycling of the injection-recovery cycle for H$_2$, in order to improve the recovery rate and purity of H$_2$ and control the recovery of CO$_2$.

In this new strategy, CO$_2$ fracturing is recommended as the technique to allow injection. First, using CO$_2$ as a fracturing fluid can generate more fractures and then increase the storage capacity due to its high fracturing efficiency (lower volume of injected fluid to generate a microseismic event), as observed in Case 7. Moreover, the higher capacities of pumps (hydraulic power) and wellheads (stress tolerance) for

![Fig. 9. Schematic of different CO$_2$ storage configurations and mechanisms in (a) conventional (both fractures and matrix) and (b) unconventional (mainly fractures) reservoirs. The matrix in unconventional shale reservoirs restrains the penetration of CO$_2$, leaving the fracture system to dominate the storage capacity – different from the conventional porous system storing CO$_2$ to inhabit both fractures and matrix.](image)

![Fig. 10. Conception of symbiotic storage of CO$_2$ and H$_2$ in shale reservoirs. CO$_2$ is used as a cushion gas to replenish the deficit of reservoir pressure for the recovery rate of H$_2$, which in return drives more CO$_2$ deeper into the shale matrix for permanent sequestration. Redrawn with permission from Ref. [86], copyright (2021) Elsevier. (This figure has been completely redesigned and redrawn by the authors of the present manuscript).](image)
fracturing, compared with the equipment for flooding or huff and puff stimulation/production, enable the high-pressure injection of CO₂, which increases the percentage retained (Figs. 3 and 6), decreases the recovery of CO₂, and eventually improves the purity and recovery of H₂. However, the proportion of CO₂ utilized in the total fracturing fluid should be increased, and ideally, should reach 100%. The pumping rate of CO₂ injection should also be increased to enhance proppant transport, fracture propagation, and fracture width [167,168]. An environmentally-friendly and high-efficiency friction reducer is also required to sustain the high-flow-rates necessary for large scale CO₂ injection [86]. The flowback rate of injected CO₂ after fracturing must also be understood and controlled [169,170]. Surface engineering is another bottleneck for fracturing using pure CO₂, including the storage of CO₂ in the field, the capacity of the sealed proppant blender, the provision of real-time supplementary CO₂ for large-scale injection and other factors [171,172]. Therefore, initial breakthroughs in CO₂ fracturing may occur in high payback but water-sensitive reservoirs.

4.4. New evaluation of the prospects of CO₂/H₂ storage in shale

Based on the prior fracture-dominant mechanism, a new evaluation method of CO₂/H₂ storage capacities is proposed based on the scale of fracturing (total volume of injected fluids) in shale reservoirs. The new method assumes that the injection volume of fluids is approximately equal to the volume of created and diluted fractures and then is equivalent to the CO₂/H₂ storage capacity – defined as the equivalent-fracturing method. This method is supported by the apparent effective impermeability of the shale matrix to fracturing fluids, as well as necessary simplifications, such as (1) ignoring the retained fracturing fluids in reservoirs and (2) ignoring the volume of adsorbed CO₂ and H₂. The storage estimate based on this new method is considered to be a minimum although the most technically achievable capacity in shale, referring to the CO₂ injection scales of Cases 1–3 in Table 1. It is also crucial in assessing the capacity of H₂ storage in shales because of the cyclic and repetitive injection and withdrawal process that, due to rapid cycling times, mainly occurs within the fracture network before wholesale diffusion into the matrix can occur.

Taking CO₂ storage as an example, this new method is applied to re-evaluate the storage capacity in Marcellus shale. The total volume of fracturing fluids in Marcellus is estimated by the water usage per fracturing well (an average value of 22,500 m³) [173–175] and the number of wells drilled annually reported by the Marcellus Center for Outreach and Research (PennState-MCOR) [176]. Thus the newly estimated CO₂ storage capacity in Marcellus shale is 466 million tons as of the year 2019, which is lower than previous estimates (Gt-level) but is still challenging to accomplish because the presumed average CO₂ storage in a single well (22,500 m³) is much larger than those in field tests (~3265 m³, Table 1). This new equivalent fracturing method assesses the technically feasible capacity of CO₂ storage in shale, which can be used as a supplement to the evaluation system, and to mitigate the contradiction between the over-estimated CO₂ storage in formation and under-estimation in a single well.

5. Conclusion

A critical review of CO₂ and H₂ storage in shale reservoirs is performed across time and spatial scales. Field cases are critically evaluated with a literature review focusing on field observations and lessons learned, which generate 24 individual lessons from both field pilots and laboratory studies (as presented in Fig. 8). Cross-analyses and validations among these various lessons are performed (as shown in Fig. 8) to demonstrate the principal features of injectivity and sealing behavior in shale reservoirs and the dominance of fracture networks in storing CO₂ and H₂. Perspectives on CO₂ and H₂ storage in shale are proposed by further analyses to pave a broader pathway to carbon neutrality and clean energy transition, which includes.

1. The fracture-dominated mechanism of CO₂/H₂ storage in shale is clarified. The more isolated nano-scale pores in shale result in a relatively impermeable matrix, in which fracture networks dominate the injection and then the storage capacity. This fracture-dominated system is cross-validated by field measurements (injecting pressures, scales of CO₂ and offset-well monitorings) in previously-fractured and initially-intact shales (Table 1) with the storage behavior of H₂ (mainly stored within fractures) defined as based on numerical simulations (Fig. 7);

2. An overestimation of CO₂ storage capacity in shale is anticipated. Volumetric and production-based methods of estimation, designed for conventional formations with highly-permeable porous media, may be inapplicable for unconventional reservoirs due to the more isolated nano-scale pores and fracture-dominant mechanisms, as compared in Fig. 9. Hydraulic injection under limited pressure and continuity can only drive CO₂ into the skin of the shale matrix blocks (Case 4 and Fig. 9 b). Furthermore, the injected CO₂ may not follow the direct reverse paths of the CH₄ production (deeply into the shale matrix driven by continuous geologic stress and pore pressure), which violates a basic assumption for the production-based method and thus results in the overestimation of potential storage volumes;

3. An underestimation of the scale of the injected CO₂ in the reported field cases is observed and is attributed to the low injecting pressure (indicating that CO₂ mainly concentrates in previously-fractured shales, Case 3) and the low proportion of injected CO₂ (in total injected fluids, Cases 6 and 7), as presented in Table 1. This may result from the unknown characteristics of the fracture networks, the greater penetration of CO₂ as a supercritical fluid and the deficits of pressure and fluids during production – principal factors affecting storage capacity. Among these factors, quantitatively evaluating artificial fractures at field scales is crucial in enhancing the scale of injection of CO₂ in a single well, which represents a promising research orientation;

4. A new strategy of integrating CO₂ storage and H₂ storage in shale is proposed and then demonstrated by using the same flow path (through fracture networks) of CO₂ and H₂ based on cross-analyses of field tests of CO₂ injection (Table 1 and Fig. 1) and numerical simulations of H₂ storage (Fig. 7). The previously stored CO₂ and remnant CH₄ in a dry gas reservoir can be used as cushion gases to maintain reservoir pressure and thus enhance H₂ recovery (Fig. 10). In this strategy, CO₂ fracturing (with an efficiency ~5 times higher than water-based fracturing, Fig. 2) is recommended for CO₂ storage to increase the fracture volume and the percentage of retention of CO₂ (Figs. 3 and 6) by the increased injecting pressure. This improves the storage capacity in fractures and permanent storage of CO₂ while also maximizing the purity of the recovered H₂. Correspondingly, further studies integrating CH₄ production, CO₂ sequestration, and H₂ injection and then production are essential to reveal the multiphase flow mechanisms in both matrix and fractures, as well as developments in the technical progress for CO₂ fracturing (friction reducer, flow-back control, and surface equipment);

5. A new equivalent-fracturing method, based on a fracture-dominant mechanism, is proposed and used as a supplement to the evaluation system to mitigate the over- and under-estimations and evaluate the prospect of CO₂ and H₂ storage in shales. Taking CO₂ storage as an example, the new method may be applied to the Marcellus shale and suggests 466 million tons of CO₂ storage capacity in artificial fractures, which is lower than previous estimates (Gt-level that considered storage in both fracture and porous matrix). This fracture-based method estimates a more technically achievable prospect considering the impermeability of the shale matrix, which may improve the injection scale of CO₂ in field pilots.
Declaration of competing interest

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

Data availability

No data was used for the research described in this article.

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