International Journal of Greenhouse Gas Control 142 (2025) 104342

Contents lists available at ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

Opportunities and challenges for geologic CO_2 sequestration in carbonate reservoirs: A review

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ARTICLE INFO

Keywords:
Climate change
Carbon dioxide (CO_2)
Carbonate reservoirs
Carbon sequestration
Geology
Saline aquifers

ABSTRACT

Within the last three decades, there has been a remarkable increase in both the adoption and implementation of geologic CO_2 sequestration, a mature and well-established method for reducing greenhouse gas emissions. Numerous research efforts have been geared toward subsurface engineering for effective containment and project scale-up in various types of geologic reservoirs, including sandstones, shales, carbonates, ultramafic, and basalts. However, only a handful of full-scale or pilot projects have been conducted in carbonate reservoirs despite their favorable petrophysical characteristics and wide prevalence across the globe. The principal challenge for CO_2 sequestration in carbonate reservoirs includes concerns surrounding the effective containment of CO_2 due to geologic complexities, such as high reactivity, petrophysical heterogeneity, structural compartmentalization, and mineralogical variability. Nonetheless, carbonate reservoirs are often characterized by porosity and permeability that are favorable for CO_2 sequestration, and they frequently occur below low-permeability cap rock. Moreover, carbonate formations are prevalent in many geologic basins worldwide and in close proximity to anthropogenic CO_2 sources. Thus, with proper engineering, carbonate formations will play a significant role in geologic CO_2 sequestration to achieve the global emissions reduction target.

This paper presents a comprehensive review of carbonate reservoirs in the context of geologic CO_2 sequestration. We explore their unique opportunities and challenges, including their geology, global distribution, and natural CO_2 accumulations. Insights are drawn from a wide range of sources, including experimental studies, numerical and reactive transport modeling, and pilot projects. We highlight the various factors that influence effective CO_2 storage, providing recommendations for successful geologic CO_2 sequestration.

1. Introduction

In the wake of the Paris Accord and the realities of climate change, there has been a growing global need to reduce emissions of greenhouse gases. Global carbon dioxide (CO_2) emission from energy-related processes increased globally by 321Mt in 2022, reaching a new peak of over 36.8 Gt (IEA, 2022). Achieving net-zero emissions by mid-century (2050) will require keeping a substantial amount of anthropogenic CO_2 from the atmosphere. Geologic CO_2 sequestration is one of the viable and mature methods to achieve this goal. The past three decades have seen a remarkable global increase in both the adoption and research efforts dedicated to the sequestration of CO_2 in geologic formations, driven by the urgency to offset these emissions. As of 2023, 40 operational commercial facilities were utilizing carbon capture, utilization, and storage (CCUS), with over 500 projects at different phases of development (IEA, 2022).

Various geologic formations have been considered for geologic CO_2 storage, including saline aquifers, depleted oil and gas fields, and carbon mineralization in basalts. Among these, saline aquifers have gained significant attention as a potential long-term storage solution for captured CO_2. Saline aquifers are prevalent throughout many sedimentary basins worldwide, and they are generally characterized by high reservoir porosity and permeability, giving them the largest potential for CO_2 storage among all options (Ang et al., 2022; Bentham and Kirby, 2005). Although global estimates for the geological storage capacity of CO_2 vary, there is a general consensus that the capacity in saline aquifers is deemed adequate for the anticipated volumes of CO_2 that require storage (Bergmo et al., 2011). Moreover, most of the world's recoverable

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https://doi.org/10.1016/j.ijggc.2025.104342
Received 19 August 2024; Received in revised form 9 February 2025; Accepted 26 February 2025

petroleum occurs within carbonate reservoirs (Baines and Worden, 2004; Jia, 2012; Lima et al., 2022), making them important future CO_2 storage sites. As of 2020, marine carbonate strata hosted about 53 % of oil and gas basins actively producing oil and gas commercially (Xu et al., 2020). Despite the prevalence of carbonate reservoirs globally, there is limited field implementation of CO_2 storage in carbonates, with few projects to benchmark against. Most of the existing underground CO_2 storage globally occurs in sandstone formations. A 2014 study by Cook et al. (2014) shows only 17 % (including enhanced oil recovery) of large-scale global projects had been conducted in carbonate reservoirs, compared to 75 % in sandstones. Notable non-enhanced oil recovery (EOR) pilot projects include the Hontomín Pilot in Spain and the Ohio River Valley CO_2 American Electric Power (AEP) Mountaineer Project in the USA, among others.

Generally, the exploitation of carbonate reservoirs for CO_2 storage is challenging due to heterogeneities at various scales, which introduces subsurface flow complexities and significant uncertainties in predicting CO_2 plume behavior (Agada et al., 2016). There are also concerns about the storage capacity and security of CO_2 arising from geochemical fluid-rock reactions that alter pore structures and fracture networks, thus affecting porosity and permeability (You and Lee, 2021). According to Gunter et al. (2000), carbonate aquifers, without the presence of basic silicate or aluminosilicate minerals, are not good mineral traps for CO_2 since carbonate reactions tend to reach equilibrium conditions rapidly. This is similar to the observation of Baines & Worden (2004), where carbonate minerals that do not contain aluminosilicate are unable to sequester secondary CO_2 due to the carbonic acid dissolution of matrix cement, rock fragment, fault seal, or top seal. These challenges, among others, have raised doubts about the effectiveness of carbonate reservoirs in effectively sequestering CO_2.

Although carbonate minerals may exhibit high reactivity in the presence of carbonated brine, it is important to note that these reactions are not always necessarily detrimental. Carbonate minerals may act as a buffer, helping to maintain a stable pH in the subsurface, thus promoting precipitation of carbonate minerals and preventing excessive rock dissolution at low pH. Although the relative percentage of mineral trapping may be low depending on the mineralogic content of the reservoir, other trapping mechanisms are equally relevant in effective CO_2 storage (Yu et al., 2015). It is also worth mentioning that carbonate rocks may contain various mineral aggregations, including silicates embedded in the rock structures, which can promote the formation of secondary carbonate. Additionally, the dissolution of carbonate rocks creates secondary pore spaces, potentially enhancing CO_2 storage capacity. Furthermore, carbonates demonstrate self-healing properties as CO_2 and brine interactions induce the precipitation of minerals like halite, dawsonite, and calcite, which are transported to fill potential leakage pathways – faults and fractures, thus minimizing the risk of CO_2 leakage, and improving the overall storage security of the injected CO_2 (Barbosa Machado et al., 2023b; Patil et al., 2017). It is a complex interplay, and the ultimate outcome depends on various geological and hydrogeological factors. The existence of natural accumulations of CO_2 in some carbonate formations points to the possible viability of engineered CO_2 storage in these systems, a phenomenon which is discussed further in Section 2.

The unique challenges of sequestering CO_2 in carbonate, including the multiple factors affecting its effective containment, require in-depth investigation. In this paper, a comprehensive review of CO_2 sequestration in carbonates is conducted, elucidating some of the challenges of geologic CO_2 sequestration in carbonate reservoirs with emphasis on saline aquifers and depleted oil and gas fields (excluding EOR). To support the rapid buildout of industrial carbon capture and sequestration (CCS) facilities worldwide, our distinctive perspective frames this review in the context of field-scale implementation. The geology of carbonates is discussed in the context of CCS, followed by discussions about storage mechanisms, injectivity, and other reservoir and physical parameters affecting CO_2 storage in carbonate formations. This discussion is followed by a review of experimental, numerical, and reactive transport research in carbonate reservoirs, and we close by drawing insights from two pilot projects that, when combined with the theoretical framework, point towards general guidelines for CCS in carbonate reservoirs.

2. Geology of carbonates

Sedimentary rocks comprising predominantly carbonate minerals are classified as carbonate rocks. The two most common types of carbonate rocks are limestone and dolostone, which are composed primarily of calcium carbonate (e.g., calcite and aragonite ($CaCO_3$)) and calcium-magnesium carbonate (e.g., dolomite $(Ca,Mg)_2CO_3$) minerals, respectively. Besides these primary carbonate minerals, other frequent constituents of carbonate rocks are siderite ($FeCO_3$) and ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$), which are also abundant in sedimentary hydrocarbon reservoirs as diagenetic authigenic cement (Abdulkarim et al., 2022; Bicocchi et al., 2017; Boles, 1978; Liu et al., 2011; Yang et al., 2018). The formation of carbonate rock originates primarily from biological activity and, to a lesser extent, inorganic precipitation, in contrast to siliciclastic reservoirs, which originate from erosion and transportation of materials from pre-existing rocks (Ahr et al., 2004). As shown in Fig. 1, carbonate formations exhibit diverse origins, including (1) **Detrital**, derived from preexisting limestone and shell fragments; (2) **Constructed**, primarily built by living organisms such as corals, algae, and other microbial processes, creating reef structures or other carbonate platforms; (3) **Chemical**, formed from the precipitation of bicarbonate mainly in marine muds; and (4) **Chalk**, formed from the accumulations of calcareous micro- and nannofossils such as foraminifera, single-celled algae (e.g., coccolithophores) (Ahr, 2008; Eyinla et al., 2023). In addition, carbonate formations are often characterized by karst features, resulting from the dissolution of limestone or dolomite by water (Larson and Emmons, 2021). The porosity and permeability of many of these rocks undergo significant alterations relatively quickly after burial, resulting in poor preservation of the original sedimentary structures (Davis, 1966). Carbonate reservoirs can pose challenges for seismic reflection techniques, primarily due to factors such as the potential absence of layering during deposition, diagenetic alterations, and issues related to structural complexity (Alcalde et al., 2014).

For carbonate formations to be suitable CCS reservoirs, there must be sufficient porosity and permeability to allow CO_2 to be injected and stored within the formation. In addition, they require the presence of effective sealing units above the target storage zone to ensure long-term CO_2 containment. Seals associated with carbonate reservoirs are commonly composed of chalks, anhydrite, salts, clays, or shales that are relatively impermeable units forming a pervasive flow barrier above and around the reservoir rock. The origin of these sealing units could be either depositional or diagenetic. Heterogeneity in carbonate reservoirs is among the most important factors that dictate the effective porosity and permeability of the reservoir and thus govern the suitability of a carbonate formation for long-term CO_2 storage on an industrial scale (Ahr, 2008; Fitch et al., 2015; James and Fitch, 2010). In carbonate reservoirs, heterogeneity ranges from microscopic to megascopic scales and could be a multifaceted variation of reservoir properties over space and time. Within this context, reservoir heterogeneity is governed by the spatial variability of reservoir properties, such as mineralogical compositions, depositional facies, grain morphology, the presence and distribution of diagenetic cement, pore type, pore volume, pore throat size distribution, fracture density and distribution (Fitch et al., 2015; Jennings and Lucia, 2001; Lucia et al., 2003; Mohammed-Sajed et al., 2024; Qi et al., 2020; Zhang et al., 2021). Over time, these reservoir properties may also evolve due to multi-stage diagenesis and metamorphism, resulting in a dynamic heterogeneous system, making it challenging to evaluate the CCS potential of a carbonate reservoir over long-term (Fitch et al., 2015). As shown in Fig. 2, the size classification of heterogeneity in carbonate reservoirs is generally described by (1) giga-scale (basin

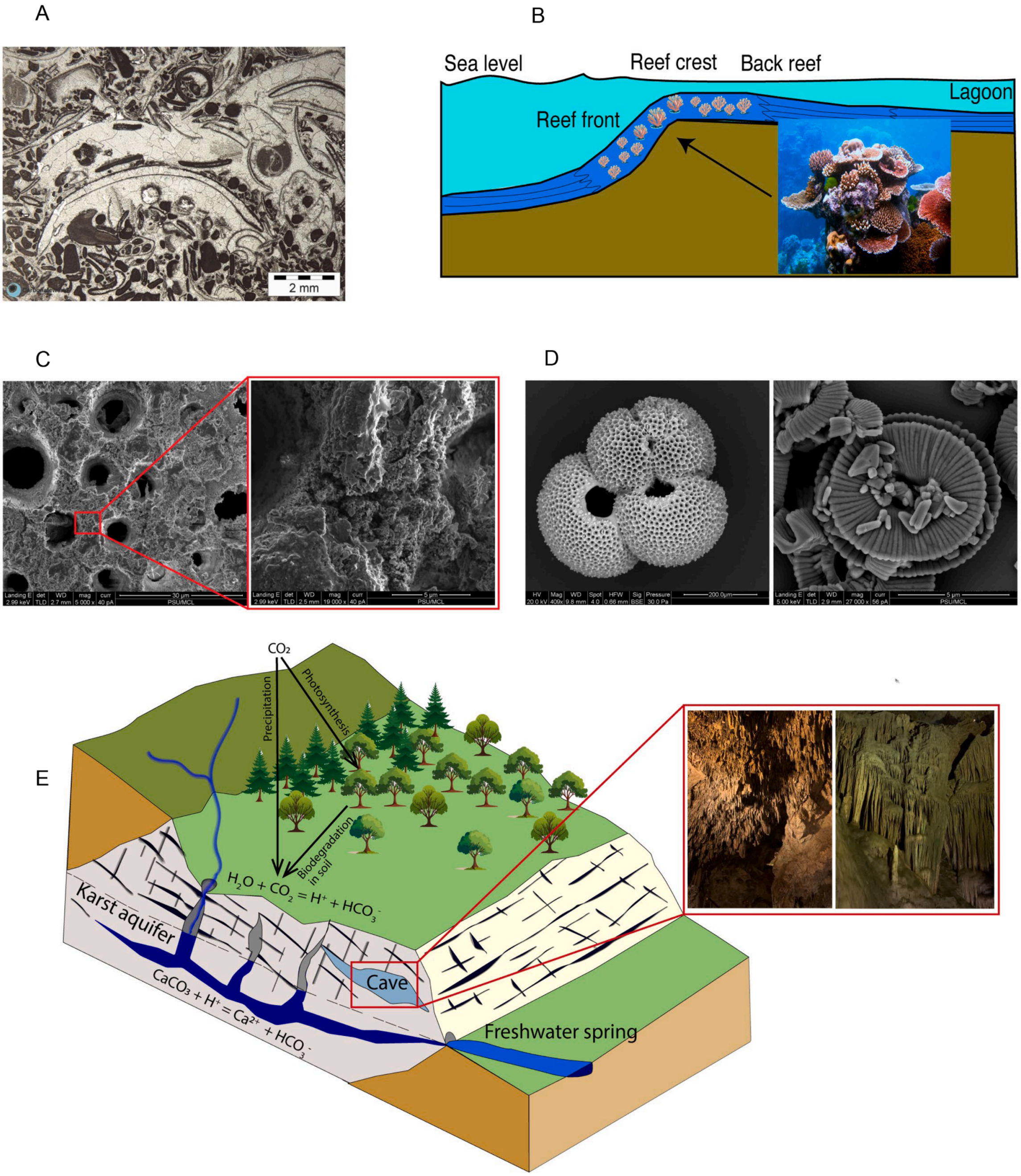

Fig. 1. Carbonates origins: (A.) Thin section photomicrograph of detrital grainstone carbonates (Della Porta and Wright, 2009); (B.) Schematic of depositional environment of coral reef as construct carbonate (modified after Della Porta and Wright, 2009) with insert photo of coral reef (Hudson, 2010); (C.) An SEM image showing authigenic calcite precipitating from pore fluids on the surface of foraminiferal tests in a deep marine core (imaged by Chanda, P.; (D.) Components of carbonate chalk: calcareous tests of foraminifera (left) and coccolithophores (right) (imaged by Chanda, P.); (E.) Schematic of carbonate karst aquifer as example of limestone dissolution (modified after Goldscheider, 2019) with inset photographs of stalactites from Dixie Cavern, Salem, VA (photographed by Chanda, P.).

scale), (2) mega-scale (reservoir scale), (3) macro-scale (facies scale), (4) meso-scale (rock lamination scale), and (5) micro-scale (pore and grain scale) (Correia et al., 2014). In the context of CCS, it is important to understand the macro- to meso-scale heterogeneities in carbonates that arise from depositional and post-depositional processes (e.g., diagenesis). These heterogeneities are detectable in the drilled cores but may be easily missed by geophysical methods such as seismic reflection imaging. However, these heterogeneities impact the petrophysical properties of the carbonate reservoirs and thus significantly influence the formation injectivity, storage capacity, CO_2 plume geometry, and CO_2 migration pattern over a longer timeframe.

Carbonate heterogeneities at the macro- to meso-scales include variations in porosity and permeability due to the presence of clay laminations or intercalations, shale/mudstone baffles, dissolution features such as cavities, macropores, vuggy porosity, micro-fractures, dolomitizations, gas chimneys, etc. Porosity in carbonates, one of the vital petrophysical properties of a reservoir, can vary from micrometer scale (e.g., microporosity in chalks and offshore carbonates) to centimeter scale (e.g., vugs) up to meter and kilometer scales (e.g., dissolution caves in karst systems). This scale-dependence of heterogeneous petrophysical properties in carbonates is often referred to as dual porosity systems with a non-uniform mixture of primary porosity (i.e., depositional) and secondary porosity (i.e., post-depositional, such as fractures, vugs, cavities, etc.) (Fitch et al., 2015; Zambrano et al., 2021).

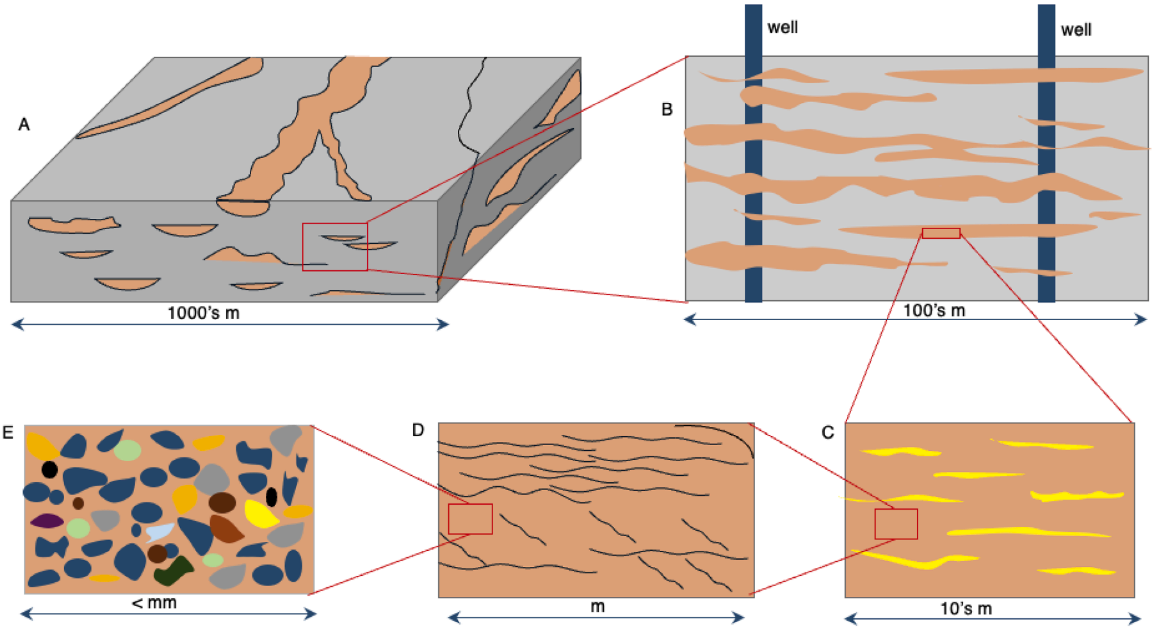

Fig. 2. Heterogeneity at various scales: (A.) giga-scale (basin scale); (B.) mega-scale (reservoir scale); (C.) macro-scale (facies scale) (D.) meso-scale (rock lamination scale) and (E.) micro-scale (pore and grain scale).

In addition to heterogeneous porosity, there are intra-reservoir lithological variations, such as the presence of shale/mudstone baffle or clay intercalations within carbonates, formed due to transition between adjacent depositional environments (e.g., change from reef carbonates to lagoonal facies (Boggs, 2012)) or post-depositional alteration (e.g., clay authigenesis during carbonate recrystallization (Baldermann et al., 2015; Chanda et al., 2023; Dunlea et al., 2017; Isson and Planavsky, 2018).

2.1. *Opportunities for CCS in carbonate formations*

The suitability of carbonate reservoirs for sequestrating CO_2 is promising. The evidence lies not only in the natural accumulations of CO_2 in carbonate formations (discussed in more detail in the subsequent section) but also in their highly porous and permeable characteristics arising from dissolution features, dual porosity/permeability systems, and connected vugs and fractures (Ahr, 2008; Guo et al., 2012; Newberry et al., 1996), which potentially translates into high CO_2 and storage capacity and injectivity. Additionally, the dissolution of carbonate rocks from reaction with CO_2 creates secondary pore spaces, enhancing their storage capacity. While existing fractures in carbonate reservoirs present a potential risk for CO_2 leakage during CCS operations, the self-sealing mechanisms involving the precipitation of secondary minerals, such as halite, dawsonite, and $CaCO_3$, can mitigate this risk by reducing fracture permeability (Barbosa Machado et al., 2023b; Patil et al., 2017). Another advantage lies in their frequent interbedding with low-permeability formations like shales and anhydrite (Alsharhan, 2006; Raup and Hite, 1992; Roberts-Ashby et al., 2015). This natural caprock configuration minimizes the potential risk of CO_2 leakage, effectively forming a combined reservoir/seal system. The presence of formation heterogeneity at different scales, a common feature of carbonate formations, could also maximize pore volume, increase residual trapping, and encourage CO_2 dissolution (Rackley, 2017; Sifuentes et al., 2009). The effect of meso- to macro-scale reservoir heterogeneity was observed in the Utsira sandstone formation in the Sleipner project where, after 10 years of injection, about 2/3 of CO_2 migrated laterally below discontinuous intra-reservoir seals reservoirs (Hermanrud et al., 2009)

Carbonate rocks are exposed across 13 % of the surface of the earth, underlying about 22 % of Europe and about 40 % of the Eastern United States (Fryar, 2021). Carbonate rocks, which constitute ~20 % of global sedimentary rocks, host the bulk of the world's recoverable petroleum and account for 70 % of global oil and gas reserves (Baines and Worden, 2004; Li et al., 2018; Xu et al., 2020), making them a huge prospective storage sites for CO_2 sequestration in both saline aquifers and depleted field. Fig. 3 shows the global distribution of carbonate karst reservoirs and their proximity to anthropogenic CO_2 sources. The extensive production history of depleted oil and gas carbonate fields not only provides valuable insights into reservoir characterization for CO_2 storage optimization but also presents the advantage of re-purposing existing oil and gas infrastructures for cost-effective storage solutions. Moreover, several CO_2-enhanced oil recovery (EOR) projects have been conducted globally in carbonate reservoirs. Some notable examples include the Uthmaniyah project in Saudi Arabia, the Northern Reef Trend project in the United States, the Weyburn-Midale CO_2 project in Canada, and Petrobras deep water pre-salt CCUS project in the Santos Basin (IPCC, 2005; Kokal et al., 2016; Pereira et al., 2024; Ganesh et al., 2021). As of 2004, 67 % of the 71 active CO_2 EOR projects in the United States were implemented in carbonate reservoirs (Manrique et al., 2007). While CO_2-EOR is beyond the scope of this review, and the storage mechanism may differ to some degree relative to CO_2 storage in saline aquifers, successful implementation of CO_2-EOR demonstrates that the technology exists to inject CO_2 in carbonate reservoirs and offers valuable insights and methodologies that can be effectively translated and applied to geologic CO_2 sequestration in saline aquifers.

Furthermore, several regional assessment studies conducted by the United States Geological Survey (USGS) have identified various storage assessment units (SAUs) in carbonate formations. These SAUs are characterized by (i) sufficient permeability and porosity for CO_2 injection and storage, (ii) laterally extensive low permeability caprock, (iii) brine concentration above 10,000 ppm dissolved solids, and (iv) depths greater than 800 m, the latter of which ensures sufficient formation pressure to inject CO_2 as a supercritical phase fluid. The USGS SAUs in carbonate formations occur in the South Florida, Arkoma, Kansas, Williston, and Kandik basins (Buursink et al., 2013, 2014; Craddock et al., 2014; Roberts-Ashby et al., 2015). For example, in the South Florida basin, the SAUs identified by Roberts-Ashby et al. (2015) include the Cedar Keys and Lawson, Dollar Bay, Gordon Pass and Marco Junction

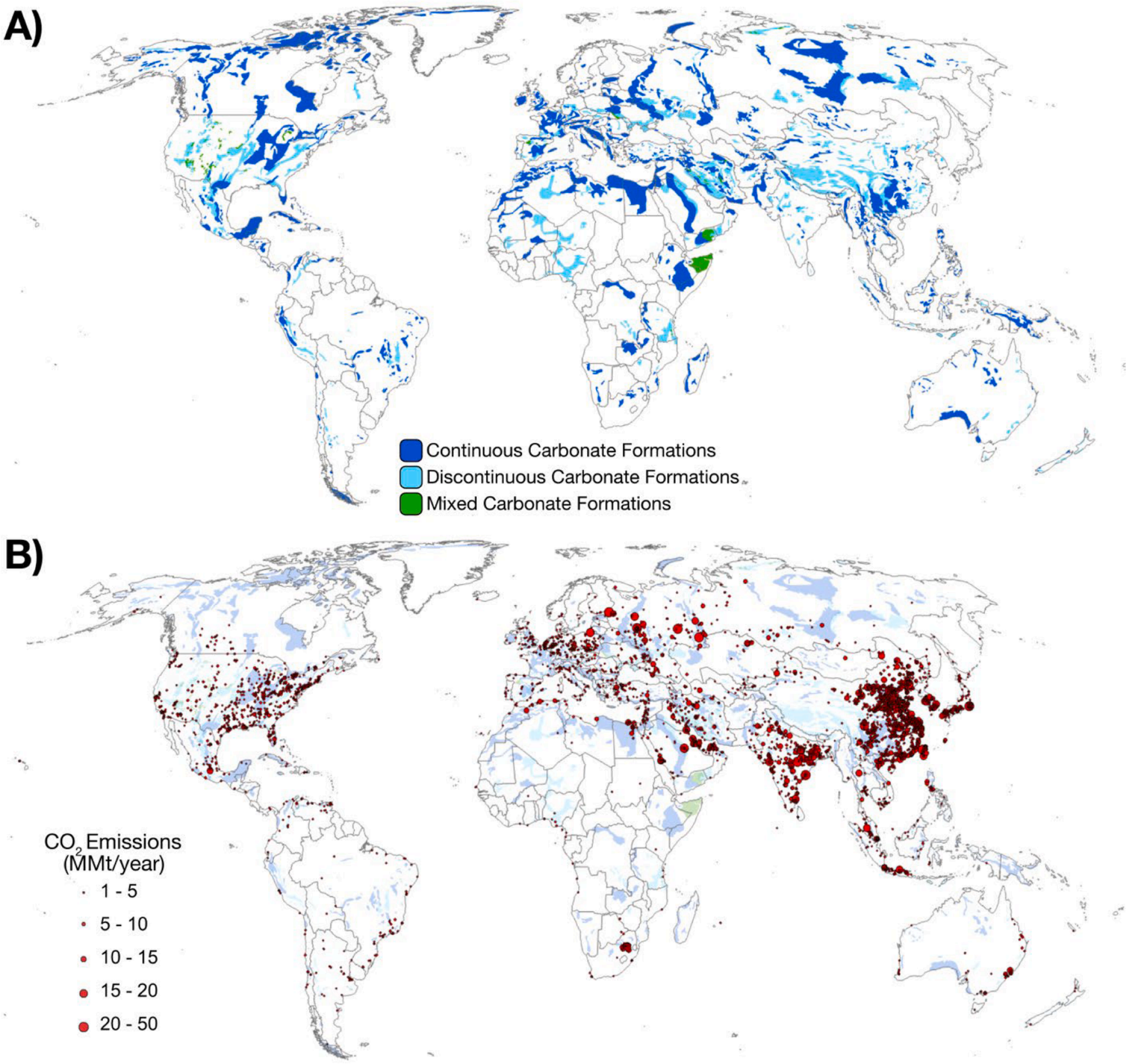

Fig. 3. (A.) Global distribution of carbonate rocks and karst water resources overlain with satellite data of CO_2. (B.) sources greater than 1 million tonnes/per year (the size of the bubble indicates CO_2 emissions level). These figures show that carbonate reservoirs are highly pervasive across most sedimentary basins and in close proximity to significant CO_2 emissions. Map modified after Goldscheider et al. (2020).

formation, Sunniland and Pre-Punta Gorda formations. These SAUs are characterized by thick successions of laterally extensive carbonate reservoirs and evaporite seals deposited in a highly cyclical depositional environment that is now the South Florida Basin (Roberts-Ashby et al., 2015). The estimated regional storage capacities of these formations are as follows: 97,000 million metric tons of CO_2 for the Cedar Keys Lawson formation, 24,760 million metric tons of CO_2 for the Dollar Bay formation, and 105,570 million metric tons of CO_2 for the Pre-Punta Gorda formation (Roberts-Ashby and Ashby, 2016; Roberts-Ashby et al., 2013), which shows a huge potential to support several large-scale CO_2 storage projects in the region. To assess the viability of CO_2 storage projects in carbonate reservoirs at industrial scale, the United States Department of Energy Carbon Storage Assurance and Facility Enterprise (CarbonSAFE) program recently announced several research and development projects in Florida and Alabama that will undertake feasibility assessment, site characterization, and permitting activities to progress towards full field implementation of CCS in saline carbonate formations.

2.2. Challenges of CCS in carbonate formations

In the context of CO_2 sequestration, carbonates pose unique challenges. Compared to silicates, carbonates are chemically more reactive in weak acids, particularly carbonic acids (Azuddin et al., 2019b; Fryar, 2021), and undergo complex geochemical reactions leading to changes in fluid composition, pH, and mineralogy. Dissolution within carbonates enlarges the pore connectivity and permeability, promotes pervasive rock dissolution, and elevates stress levels within the rock structure (Agada et al., 2016; Bell, 2005; Kovacs et al., 2015). Although large-scale dissolution caves and cavities are identifiable in subsurface seismic imaging, detecting the presence of centimeter-scale vuggy porosity in seismic reflections is challenging. There are several cases where effectively connected porosity estimates can vary by order of magnitude or more when considering microscale matrix porosity versus meso-scale fracture porosity in carbonates, causing difficulties in accurately estimating reservoir storage capacity and fluid migration properties (Akbar et al., 2000; Panza et al., 2019; Safa et al., 2021; Wennberg et al., 2016). The reaction between the CO_2-brine and the reservoir matrix could also induce mineral dissolution, affecting the porosity and permeability post-injection (Castro et al., 2019; Mouallem et al., 2023; Raza et al., 2017; Seyyedi et al., 2020; You and Lee, 2021; Zareei et al., 2022). Such factors could also significantly impact the estimation of reservoir storage capacity, prediction of plume geometry, and migration pathways of CO_2 in carbonate reservoirs (Sohal et al., 2021; You and Lee, 2021). Chemically induced effects also impact the mechanical strength of carbonates and might potentially compromise formation and caprock stability. Within a small section of a reservoir, carbonate rocks often exhibit significant variability in rock properties, as wells as heterogeneity at different scales (Fig. 2), leading to difficulties in characterization, and a high degree of uncertainty in flow prediction (Kovacs et al., 2015; Sorensen et al., 2014). Furthermore, they exhibit high levels of compartmentalization, and are characterized by the presence of natural fractures, faults, and other structural complexities. In the presence of CO_2-acidified brine, the fractured apertures in carbonates can erode quickly, affecting the integrity, flow behavior, and containment of CO_2 (Ellis et al., 2012).

2.3. *Natural accumulations of CO_2 in carbonate rocks*

The existence of natural accumulations of CO_2 in carbonate reservoirs offers insights into the potential for storage in these rock types. These natural systems have attained geochemical equilibrium and stability over very long timescales. Compared to natural systems, geomechanical deformation during engineered injection is significantly more pronounced, with the injection well penetrating these formations and injecting CO_2 at a high flow rate (Johnson et al., 2004). Nonetheless, these naturally occurring CO_2-carbonate formations offer an opportunity to investigate the behavior and extended consequences of CO_2 over time. Allis et al. (2001) conducted an extensive study of the reservoir properties of natural CO_2 reservoirs in the Southern Rocky Mountains and Colorado Plateau of the United States. The key findings from the study are: (1) natural CO_2 accumulations are structurally similar to conventional natural gas reservoirs, often found in dome-like structures. Stacked reservoirs are common, suggesting vertical migration of CO_2 through the sedimentary column of the reservoirs. (2) Dolomite and sandstones are the most common reservoir lithologies, with mudstones and anhydrite as the most common seals, which is a similar configuration to traditional reservoir/seal systems that are targeted for CCS development. (3) CO_2 concentration in the carbonate reservoirs ranges from 66 to 99 %, suggesting that carbonate reservoirs offer secure structural trapping characteristics. Pore fluid chemistry varies with depth and location, influenced by factors such as lithology and meteoric water movement. (4) The CO_2 stored in these reservoirs varies from 1 to 100 trillion cubic feet (~28.3 to 2830 billion cubic meters), with typical values ranging between 1 and 10 trillion cubic feet (~28.3 to 283 billion cubic meters). (5) There is observable evidence of natural CO_2 leakage to the surface, as indicated by the formation of travertine and geysers in some locations. Although geologic CO_2 reservoirs are widespread and there is evidence of active CO_2 flux to the surface, limnic eruptions are the only known hazards associated with surface accumulations of CO_2 (Cotel, 1999). Table 1 shows the properties of some natural CO_2 accumulation in carbonate reservoirs.

While natural CO_2 accumulations in carbonate formations demonstrate their potential for CO_2 storage, natural CO_2 seeps offer insights into the processes that may promote leakage from an engineered CCS reservoir. An analysis of leakage from natural CO_2 systems by Miocic et al. (2013) identified several mechanisms/conditions that promote leakage from CO_2 reservoirs. These conditions include shallow depth (less than 1000 m), CO_2 in less dense gas phase (versus denser supercritical CO_2), which exerts higher stresses on overburden due to buoyant forces and hydrostatic overpressure. Miocic et al. (2013) recommend storage of denser CO_2 phase, in reservoirs with less than 50 % lithostatic pressure and geopressured overburden. An analysis conducted by Lewicki et al. (2006) found that in various rock types, pre-existing fracture networks, pressure-induced fracture dilation, and shear offset induced by seismicity are the primary pathways for CO_2 migration. In one carbonate reservoir in the same study, groundwater acidified by CO_2 and H_2S led to rapid dissolution within a fault, thus increasing the natural permeability and facilitating CO_2 leakage (Lewicki et al., 2006). These natural systems, however, operate on much longer geological timescales. Further studies are required to quantify the leakage timescales in comparison to engineered CO_2 storage systems, which have shorter injection timelines and different geo-mechanical deformation processes.

3. Thermo, hydraulic, mechanical and chemical processes

3.1. *CO_2 trapping in carbonates*

Several authors have extensively investigated the mechanisms involved in trapping CO_2 in subsurface formations. These include structural trapping by impermeable seal, residual trapping by capillary forces, solubility trapping by CO_2 dissolution in brine aided by density difference between supercritical CO_2 ($scCO_2$) and brine, and mineral trapping by reaction of CO_2 with minerals to form stable carbonate minerals (Bachu et al., 1994; Gunter et al., 2004; IPCC, 2005; Rackley, 2017; Ringrose, 2023). The main storage mechanism is structural trapping, while residual and dissolution processes can be particularly significant in the injection phase (Iglauer et al., 2015). On the other hand, mineral trapping is considered the safest, most permanent, and most stable sequestration method over a geologic time scale (Massarweh and Abushaikha, 2024; Perkins and Gunter, 1995; Sun et al., 2023). These trapping mechanisms play a crucial role in ensuring the long-term storage and containment of CO_2. However, it is important to note that depending on the geology of the reservoir and the project phase, i.e., injection vs post-injection, the relevance and dominance of these

Table 1
Natural CO_2 accumulations in carbonate reservoirs. Data sources (Allis et al., 2001; Amin and Azuddin, 2016; Aydin and Merey, 2021).

Field/Site	Lithology Reservoir (R) Seal (S)	Depth (m)	Thickness (m)	Porosity (ϕ)/ Permeability (k)	CO_2 Concentration	Reserves TCF (BCM)
Big Piney – La Barge Area. Wyoming, USA	R: Dolomitized Limestone		136	ϕ: 6–12 % k: n/a	66 %	134TCF (3800 BCM)
Gordon Creek. Utah, USA	R: Limestone S: Shale & Siltstone	3340	7	ϕ: 6–12 % k: n/a	99.5 %	–
Escalante Utah, USA	R: Limestone S: Dolomite	787	120	ϕ: 6–12 %	–	–
Escalante, USA	R: Limestone & dolomite S: Shale	691	25	–	–	–
McElmo. Colorado, USA	R: Limestone S: Salt	2100	90	ϕ: 3–20 % k: 23–200mD	98.2 %	17TCF (480BCM)
AB field* Offshore Sarawak, Malaysia	R: Carbonate	1700 - 2300	500	ϕ: 15.5- 30.1 % k: 35–300 mD	78 %	–
Dodan, Turkey	R: Carbonate	850 – 2050	–	ϕ: 3–6 % k: 10–20 mD	90 %	0.5 TCF (14BCM)

* Real name of field not published by author
TCF: Trillion cubic feet
BCM: Billion cubic meters.

mechanisms can vary.

In the case of carbonates, dissolution and mineral trapping mechanisms hold particular significance due to their unique characteristics, including their high reactivity with acids and distinct mineral composition. CO_2 injected into saline reservoirs dissolves in the water present in rock pores to form carbonic acid, which dissolves rock minerals. As carbonate rocks dissolve, the pore geometry and connectivity continuously change (Agrawal et al., 2017; Ang et al., 2022) which in turn affects the amount of dissolved and trapped CO_2 by capillary forces (Krevor et al., 2015; Yang et al., 2020). Rapid dissolution of host rock minerals (mainly calcite) also occurs, producing aqueous bicarbonate species. The bicarbonate species not only lead to dolomite precipitation (Barbosa Machado et al., 2024), but also swiftly act as effective buffers, elevating the pH of the dissolved CO_2-water mixture back to a state of near-neutral or slightly alkaline, thereby checking excessive carbonate rock dissolution (Kovacs et al., 2015). Once the reservoir brine becomes saturated with CO_2, the injected CO_2 will remain as a gas phase, leading to an increase in fluid pressure (Baines and Worden, 2004), and the dissolution rate slows down and is subsequently controlled by diffusion and convection rates (Zhou, 2011). Thus, the newly injected CO_2 quickly reaches chemical equilibrium with the in-situ pore fluid, resulting in slow reaction rates (Ringrose, 2023). Consequently, this process leads to a more benign impact of the CO_2-charged plume moving through the system (reduced reactivity), and depending on the conditions, dissolved CO_2 can remain in solution or precipitate out as a new carbonate mineral (Tsar et al., 2013). This precipitation occurs as a result of an increase in cations, particularly Ca^{2+}, triggered by carbonate dissolution, leading to a localized oversaturation of the solution with carbonates (Randi et al., 2017). Overall, while some reactions, such as the precipitation of CO_2 into secondary carbonate minerals, can enhance containment, others may lead to mineral dissolution, creating pathways for fluid migration and potentially compromising containment integrity (Rochelle et al., 2004).

3.2. Effect of heterogeneity

The meso-scale shale/clay layers within reservoirs that are unresolvable in seismic reflections could also introduce unexpected impermeable zones or preferential flow paths that could impact reservoir potential for CCS (Kuuskraa et al., 2009; Santi, 2019; Wethington et al., 2022). For instance, in the Sleipner Carbon Capture and Storage, it was observed that the CO_2 plume did not rise uniformly but instead exhibited unpredictable dynamics influenced by the complex geological characteristics of the reservoir (Neufeld and Huppert, 2009). The post-injection seismic surveys and well cores revealed that such peculiar plume geometry was due to the presence of a series of thin intra-reservoir shale baffles ($\sim$1 m thick) that were not resolvable in the seismic images prior to the injection (Chadwick et al., 2004; Koehn et al., 2023; Santi, 2019). This observation closely aligns with the role multilayered stratigraphic systems with discontinuous barriers play in dispersing, immobilizing, or slowing the vertical migration of injected CO_2 as extensively discussed by Bump et al. (2023). Moreover, intraformational clay/shale baffles in saline aquifers are known sources of divalent cations (Ca^{2+}, Mg^{2+}, Fe^{2+}) that could react with the CO_2-brine and precipitate carbonate minerals, thus effectively trapping CO_2 by carbon mineralization (Mishra et al., 2020; Mishra and Haese, 2018). Similar lithological heterogeneity also exists in carbonate reservoirs, such as those in the Middle East (Verma et al., 2007; Xinmin and Li, 2018), and could potentially influence the CO_2 storage capacity, plume geometry, migration pathways, etc. In addition, the presence of meso-scale features such as mineralogical changes (e.g., anhydrite, dolomite, siderite lenses) and stylolite zones (pressure dissolution) within carbonate formation could alter the matrix-mineral dissolution rates, diagenetic reaction fronts (e.g., calcite recrystallization, dolomitization), porosity, and permeability of the reservoir and thereby impact the overall capacity for CO_2 storage over the long term (Gomez-Rivas et al., 2022; Zhou and Zeng, 2014).

Carbonate matrix heterogeneity can also have a significant impact on the migration and trapping of CO_2, affecting the storage capacity and the long-term safety of geological CO_2 storage. It can result in CO_2 flow concentrating in high permeability streaks as well as accumulating behind lower permeable layers (Trevisan et al., 2017). Using a sandbox experiment, Trevisan et al. (2017), found that compared to homogeneous geologic media, heterogeneous media lead to extended displacement times, limited vertical plume migration, and immobilization of a larger non-wetting phase fraction. Sohal et al. (2021), in their study of the effects of heterogeneity on storage capacity and CO_2 plume in fractured carbonates, found that matrix heterogeneities effect on storage capacity is substantially higher by up to 2.8× relative to CO_2 plume migration. The reservoir storage capacity decreased with increasing permeability while increasing with an increase in porosity heterogeneity. They also found that vertical migration in heterogeneous cases is reduced compared to homogeneous reservoirs, similar to the observation of Trevisan et al. (2017). Throughout the injection and migration process, CO_2 is driven upward by buoyancy forces and through high permeability streaks by viscous forces; at the same time, access to smaller pores is prevented by capillary forces (Krishnamurthy et al., 2022). In addition, carbonate mineral dissolution induces changes in pore geometry and connectivity (Agrawal et al., 2017), the magnitude of which is greater around the wellbore where stronger geochemical disequilibrium takes place, and lower at the far-field with more uniform flow regimes (André et al., 2007). Carroll et al. (2013), found that accurately predicting porosity changes from carbonate mineral dissolution requires detailed characterization of the void space – particularly 3D permeability characterization, which governs the initial transport of reactive fluids, mineral dissolution, and fluid transport into the newly created void spaces. Hence, heterogeneity in carbonates can either aid CO_2 storage by plume dispersion or lead to CO_2-front non-conformance by excessive channeling through high permeability streaks. It is therefore important to extensively characterize carbonate reservoirs in order to quantify the effect of heterogeneity on CO_2 storage in carbonates and improve overall storage efficiency. A detailed assessment of the CCS potential of the carbonate reservoir requires 3-D mapping of the intra-reservoir heterogeneity with more advanced high-resolution seismic inversion techniques, analysis of seismic attribute combinations, along with core analysis using scanning electron microscopy, computerized tomography, and nuclear magnetic resonance (Chen et al., 2021; Hendry et al., 2021; Seyyedi et al., 2020).

3.3. Effects of pressure, temperature and salinity

Pressure, temperature, and salinity all have significant effects on the fluid thermodynamic behavior, the rate of geochemical reactions, rock properties, and overall storage and containment of CO_2 in carbonate rocks (Bodnar et al., 2013; Kim et al., 2018). The pH of the solution that forms from the dissolution and ionization of carbonic acid depends on the partial pressure of CO_2, temperature, alkalinity, and salinity of the water (Sun et al., 2023). In carbonates, the solubility as well as the reaction kinetics increase substantially with decreasing pH (Renard et al., 2005). However, a numerical study to assess the mineral trapping of CO_2 in Arabian carbonates by Mouallem et al. (2023), found pH exceeding the acidic range favors mineral trapping, peaking at pH of 9 and decreasing remarkably as pH decreases (Fig. 4). The authors, however, noticed an anomaly at pH of 2, which requires further investigation. A study by Barbosa Machado et al. (2023b), revealed that CO_2 injection reduces pH levels both near the injection well and across the aquifer. The initial aquifer pH significantly influences the extent of this pH decrease. Their results also indicate that the formation of dawsonite, a secondary carbonate mineral, is favored in alkaline conditions (higher pH), and does not occur in acidic environments. Also, elevated pressure causes an increase in CO_2 solubility (Salem et al., 2013), which leads to acidification and the dissolution of calcite (Renard et al., 2005), especially around the wellbore where pressures are highest. As pressure

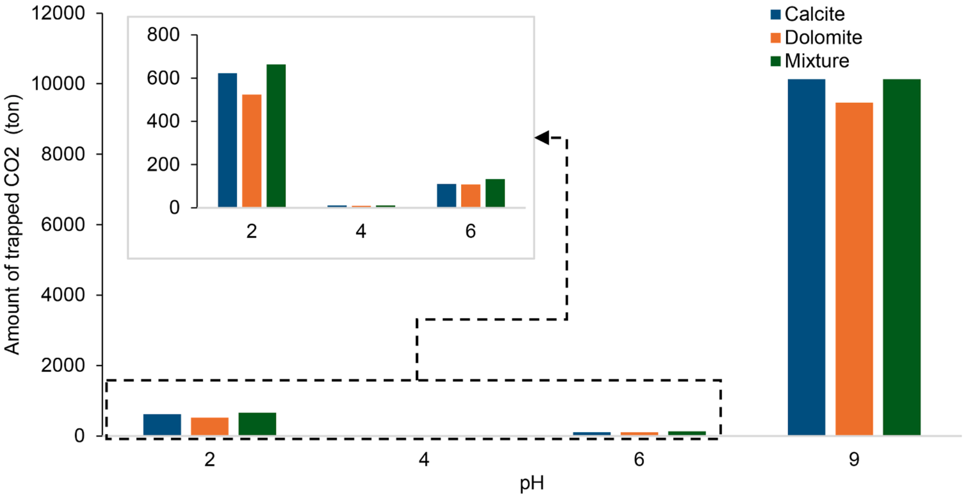

Fig. 4. CO_2 trapping capacity as a function of pH. Modified after (Mouallem et al., 2023). The results indicate that at higher pH, more CO_2 is trapped. Below pH of 7 (acidic region), amount of CO2 trapped decreases significantly.

decreases with distance from the wellbore along the flow paths, the precipitation rate of $Ca(HCO_3)_2$ and NaCl results in variations in rock properties (Izgec et al., 2005), including potential reduction of permeability in the far field. However, the pressure differential effect on calcite dissolution will decrease with increasing temperature (Xie et al., 2023).

Calcite exhibits retrograde solubility, meaning that its solubility increases with decreasing temperature and vice versa (Renard et al., 2005). Similarly, according to Henry's law and Van 't Hoff equation, CO_2 solubility decreases with increasing temperature (Carrero, 2024; Carroll et al., 1991). The reaction kinetics of dissolution and mineralization are controlled by temperature. Near the well, the injected CO_2 expands and cools by the Joule-Thomson effect (Jayne et al., 2019), which leads to increased carbonate mineral solubility, although this occurs at slower chemical reaction rates and shorter residence times, hence limiting the extent of dissolution to some degree (Azuddin et al., 2019b). However, low reaction rates due to low temperatures can be compensated by higher flow rates (Xie et al., 2023). High-pressure injection of CO_2-saturated brine into a high-temperature formation induces the formation of preferential flow pathways and releases divalent cations (Ca^{2+}) for subsequent mineral trapping (Xie et al., 2023). A numerical study by (Fathy et al., 2023b) found a 52 % increase in CO_2 mineralized by calcite as reservoir temperatures increased from 36 °C to 100 °C due to increasing reaction rates at higher temperatures. Similarly, Kumar et al. (2005) found that after 1000 years, the overall quantity of CO_2 sequestered increases with temperature at a constant salinity. In general, mineral solubility and dissolution are competing forces at low or high temperatures. At low temperatures, for example, carbonate mineral solubility is higher, while reaction rates are slower, resulting in moderate calcium and magnesium effluent (Azuddin et al., 2019b).

In both carbonate and sandstone reservoirs, CO_2 solubility decreases with increasing in salinity (Izgec et al., 2008; Salem, 2013). However, the decrease in solubility due to an increase in salinity can result in an overall decrease in mineral trapping in carbonate reservoirs, as indicated by (Fathy et al., 2023b), where an increase in salinity from 106, 069 to 170,000 ppm results in a 34 % decrease in the amount of CO_2 trapped by calcite. However, they found that changes in salinity did not impact dolomite. Brine composition also plays a role in mineral trapping, with $MgCl_2$ apparently leading to higher trapping in calcite (40.2 %) and dolomite (92.1 %) compared to NaCl at 100,000 ppm in a study conducted by Mouallem et al. (2023).

3.4. Multi-phase fluid dynamics

Rock-fluid interactions, including wettability, relative permeability/hysteresis, and capillary pressure/hysteresis, can also impact storage efficiency in carbonates. CO_2 storage is controlled by the phase behavior of the CO_2-brine, which in turn depends on brine salinity, temperature, and pressure, while the CO_2 storage as an immobile phase depends principally on the relative permeability and non-wetting phase residual saturation, which are rock dependent (Kumar et al., 2005). Structural and residual trapping are significantly affected by wettability during the first several centuries in a storage project (Iglauer et al., 2012). In carbonate and clay minerals, there are circumstances that may give rise to partial wetting of CO_2 in contrast in sandstones which are generally assumed to be non-CO_2 wetting (Ringrose, 2023). Limestones with pure calcite mineralogy are strongly water-wet in CO_2-water systems, while oil-wet limestone is intermediate- or CO_2-wet in CO_2-water systems (Iglauer et al., 2015). These lower water-wet conditions can lead to increased CO_2 mobility, potentially extending CO_2 plumes and influencing the area-of-review for permitting, while also increasing fluid pressure on caprocks (Iglauer et al., 2015). In oil-wet reservoirs, residual trapping can be relatively low. For example, Baban et al. (2023) used a nuclear magnetic resonance (NMR) experimental study of CO_2-oil sandstone to observe a significant increase in residual CO_2 saturation in water-wet (20 %) vs oil-water wet (12 %) after 20 pore volumes were injected. Chaudhary et al. (2013) observed a 15 % and 2 % trapping in water-wet and oil-wet, respectively. Similarly, Al-Menhali & Krevor (2016) found that $scCO_2$ residual trapping in a limestone, which was altered by oil to a mixed-wet state, was notably lower in contrast to an unaltered water-wet rock. A numerical study conducted by Fathy et al. (2023a) in a depleted carbonate gas formation found a monotonic increase in mineral trapping with wettability change from strongly water-wet to intermediate water-wet, irrespective of reservoir heterogeneity. They found a more lateral and upward growth of CO_2 in intermediate water-wet systems versus water-wet conditions.

The irreducible water saturation and residual CO_2 saturation also influence the storage capacity of geological formations, and they are highly dependent on rock types (Ringrose, 2023). During the injection as well as the post-injection phases of CO_2 injection into brine reservoirs, capillary forces and wettability play a very important role in CO_2 storage capacity (Tokunaga and Wan, 2013). After CO_2 injection ceases, the residual saturations resulting from fluid displacement are influenced by absolute and relative permeabilities, as well as hysteresis and other factors (Kumar et al., 2005). In strongly water-wet systems, hysteresis effects are significant in the non-wetting (CO_2) relative permeability only (Juanes et al., 2006). Relative to sandstones, carbonates may be more prone to relative permeability hysteresis due to heterogeneity and a high degree of their pore structure alteration by fluid flow. At the time of this writing, there remain substantial knowledge gaps in numerical modeling frameworks for relative permeability and capillary pressure effects in CO_2-wet and intermediate-wet conditions, and we highly recommend future research aimed at improving the ability to predict CO_2 mobility in these mixed-wetting conditions.

3.5. *Fluid-rock geochemistry*

Various authors have conducted extensive laboratory experiments providing valuable insights into understanding carbonate rocks during exposure to $scCO_2$ and carbonated brine. These include, among others, increase or decrease in porosity, increase or decrease in permeability (Ellis et al., 2013; Izgec et al., 2008; Izgec et al., 2005; Mohamed et al., 2010; Zareei et al., 2022), formation of wormholes and focused flows through high permeability channels (Al-Dhafeeri et al., 2023; Luquot et al., 2014; Selvadurai et al., 2017; Zareei et al., 2022), and formation drying and brine desiccation around the injection well (Rosenbauer et al., 2005). These changes are driven principally by carbonic acid-induced carbonate rock dissolution, transportation, and deposition of rock minerals and precipitates. For more detailed experimental reviews of pore-scale processes, see Siqueira et al. (2017), Raza et al. (2020), and Eyinla et al. (2023). These observations by different authors indicate that the resulting petrophysical property changes depend on several complex interacting factors including rock mineral composition, fraction of insoluble minerals in the matrix, initial pore structure, CO_2 concentration, pressure, temperature, salinity, injection rates or flow regime, formation water initial composition (Egermann et al., 2005); Eyinla et al., 2023; Hao et al., 2015; Izgec et al., 2008; Rosenbauer et al., 2005; Zareei et al., 2022;

As depicted in Fig. 5 above, the chemical processes that occur in the reservoir are highly dependent on the supercritical CO_2 saturation (André et al., 2007). When CO_2 first enters a storage formation, the CO_2 saturation is low, e.g., less than ~0.05; however, this free-phase CO_2 dissolves into the formation brine causing a rapid drop in pH, which drives carbonate dissolution and potentially increases porosity. As CO_2 injection continues, the saturation may exceed ~0.8, which is thought to encourage carbonate precipitation in micropores, perhaps because the remaining brine becomes supersaturated with respect to carbonates. Without incorporating reactive transport, experimental and numerical studies that only address flow properties are of limited use in understanding these phenomena (Siqueira et al., 2017). Reactive transport studies couple the transport of CO_2 with its resulting geo-chemical reactions i.e., advection-diffusion, dissolution-precipitation, and thermodynamics, for enhanced understanding of the complex interactions of rock-fluid over time, CO_2 dissolution, assessment of long-term CO_2 security by mineral trapping, including associated potential containment risks (Randi et al., 2017; Smith et al., 2013; Xu et al., 2011). The outcome of reactive transport models can differ significantly depending on the type of rock minerals involved, whose rates of reactions are dependent on rate constants as well as the mineral surface area (Kweon and Deo, 2017; Noiriel et al., 2009), including experimental and numerical thermodynamic conditions and parameters employed. Relative to sandstone, which consists of silicate minerals, carbonate rocks consist mainly of calcite and dolomite which readily dissolve and precipitate under specific chemical conditions, with faster reaction expected in calcite than dolomite (Azuddin et al., 2019b; Pokrovsky et al., 2009). This high reactivity causes rapid dissolution and precipitation of the

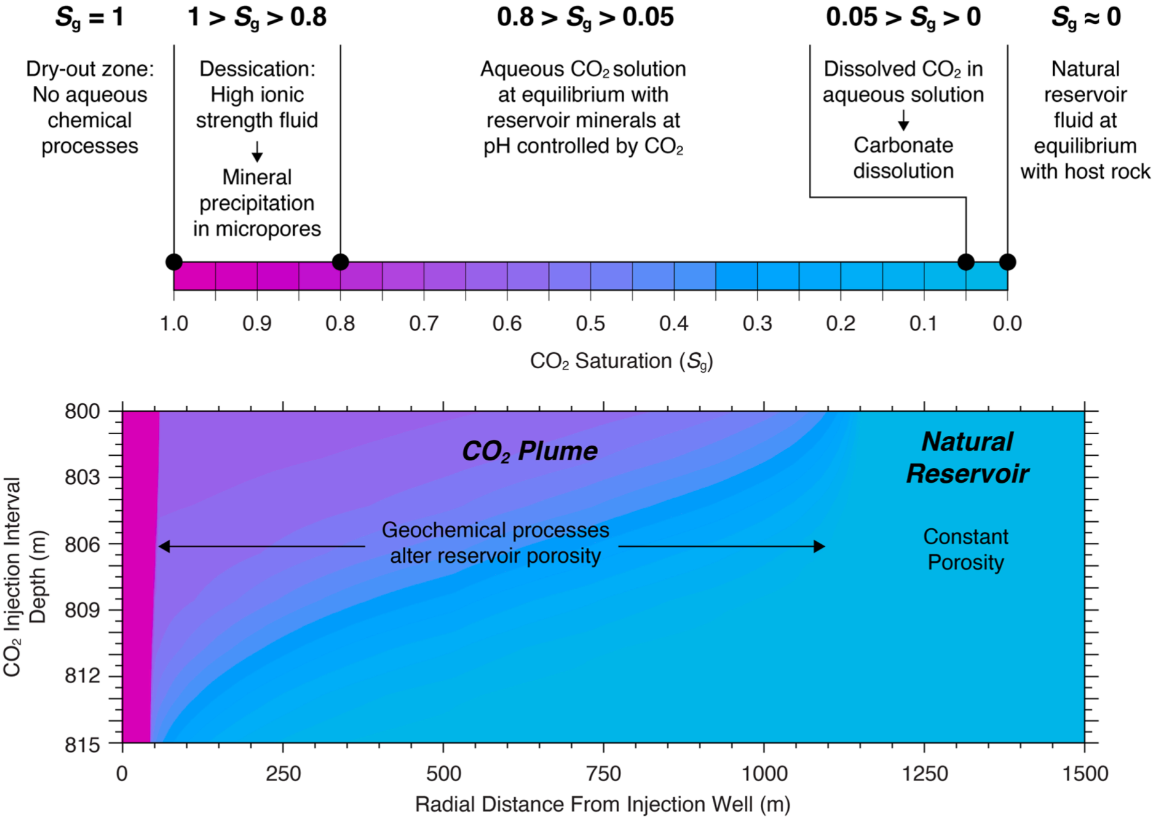

Fig. 5. Diagrammatic depiction of geochemical processes involved in CO_2 injection into a carbonate reservoir. At CO_2 saturation (S_g) less than ~0.05, carbonate dissolution is likely to increase porosity as CO_2 dissolves in formation brine, thus decreasing pH; whereas, S_g greater than ~0.8 may favor carbonate reprecipitation in micropores (André et al., 2007). To illustrate the relationship between CO_2 plume architecture and S_g, the lower panel presents results of a 2-D radially symmetric CO_2 injection simulation, where low S_g, and thus mineral dissolution, would occur at the leading edge of the plume, while higher S_g, and thus mineral precipitation, occurs nearest the injection well and top of the reservoir.

carbonate rock mass, and may have significant influence on the porosity, permeability, and geochemical conditions of these rocks (Agrawal et al., 2017). Specifically, carbonate strata with high calcite content are prone to secondary pore formation due to preferential dissolution of calcite in acid fluids, while gypsum and anhydrite are less susceptible (Peng et al., 2018). For example, André et al. (2007) found that the injection of acid solution dissolves carbonates (calcite, siderite, and dolomite) more readily than aluminosilicates (albite, K-feldspar, and illite), followed by the precipitation of siderite and calcite further downstream. They also found minimal porosity changes from albite and K-feldspar dissolution compared to carbonate mineral dissolution. Calcite minerals, which react in moderate to high CO_2 partial pressures and high alkaline solutions, can eventually be mobilized, transported via convective flow, and precipitated in the far-field, thus storing CO_2 in stable solid form (Amin and Azuddin, 2016). It is worth mentioning that the petrophysical changes at field scale may differ compared to laboratory experiments. For example, the results of reactive transport simulation calibrated with laboratory experiment data of a depleted carbonate gas field by Azuddin et al. (2019a) show that porosity changes at field scale is one order of magnitude lower than laboratory-scale. They attributed the disparity to the potentially limited mineral contact with acidified brine and higher resident time from lower injection flow rate at laboratory scale. Table 2 provides a summary of reactive transport study outcomes reported by various authors.

The equations below show the mineralization process of calcite and dolomite minerals. First, CO_2 dissolves in-situ in water to form carbonic acid (H_2CO_3) followed by a dissociation into hydrogen ion (H^+) and bicarbonate ion (HCO_3^-) or carbonate ions (CO_3^{2-}). This is followed by rock mineral dissolution releasing divalent cations (e.g., Ca^{2+}, Mg^{2+}), which react with bi-carbonate ions to permanently fix carbon as secondary carbonate mineral rocks (Xie et al., 2023).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$$

$$Dolomite\ (CaMg(CO_3)_2) + 2H^+ \leftrightarrow 2HCO_3^- + Ca^{2+} + Mg^{2+}$$

$$Calcite\ (CaCO_3) + H^+ \leftrightarrow HCO_3^- + Ca^{2+}$$

$$HCO_3^- + Ca^{2+} \leftrightarrow CaCO_3 + H^+$$

$$HCO_3^- + Mg^{2+} \leftrightarrow MgCO_3 + H^+$$

CO_2 mineralization is generally a slow and time-dependent process (Raza et al., 2020). The timescale varies depending on mineral compositions and their dissolution rates (Xu et al., 2001), and typically occurs faster with carbonate minerals. However, in carbonate reservoirs, the percentage of CO_2 trapped by calcite and dolomite mineralization from numerical studies (Amin et al., 2022; Gunter et al., 2000; Xu et al., 2001) is relatively very small or negligible compared to other storage mechanisms. This is due to the pH buffering effects of carbonate minerals leading to an overall decrease in mineral dissolution rate. In addition, carbonate reactions tend to reach equilibrium conditions rapidly, and without the presence of silicate and aluminosilicate minerals, carbonates are not generally considered to be favorable for CO_2 mineral trapping (Baines and Worden, 2004; Gunter et al., 2000).

The presence of impurities in the CO_2 stream, such as nitrogen (N_2), oxygen (O_2), sulfur oxides (SO_x), hydrogen sulfide (H_2S), and argon (Ar) can significantly influence the efficiency of CO_2 sequestration in several ways. While the co-injection of these impurities with CO_2 reduces the overall capture and processing cost (Lu et al., 2016; Wang et al., 2015; Zhang et al., 2024), these impurities impact the CO_2 phase behavior, density, viscosity, solubility, fluid flow, storage capacity, and leakage (Coelho et al., 2015; Rackley, 2017; Yu et al., 2023). As extensively discussed in the preceding sections, carbonate reservoirs are highly reactive to acidic components in the CO_2 stream. Impurities such as SO_x and H_2S can dissolve in water to form acidic solutions, which enhance the dissolution of carbonate minerals. While this can increase porosity and injectivity in the short term, it may also lead to mechanical instability of the reservoir, especially around the wellbore. Moreover, a numerical study by Seisenbayev et al. (2023), found that despite rapid mineral dissolution of minerals due to the presence of H_2S-O_2, the reservoir porosity decreased with increasing volume fraction of the impurities suggesting that the precipitation of anhydrite resulting from H_2S–O_2 co-injection outweighed the dissolution of minerals. Furthermore, the presence of non-reactive impurities like N_2, O_2, and Ar reduces the density as well as the viscosity of the mixture stream, which in turn reduces the amount of CO_2 structurally trapped as a result of the fractional volume occupied by these impurities as well as a decrease in density (Rackley, 2017). An experimental study by Lu et al. (2016) investigated the impact of impurities in carbonate reservoirs. The study found that the presence of 3.5 % O_2 in the CO_2 stream had an insignificant effect on the reactivity of limestone. However, in dolomite, the O_2 in the presence of ankerite and silicates led to the formation of iron hydroxide. Nevertheless, their results indicate no significant negative impact of O_2 to carbonate reservoirs. Pearce et al. (2015) found that the presence of carbonate minerals buffers the low pH due to SO_2 dissolution in brine. The study also found that if SO_2 migrates to the carbonate seal, there is a high likelihood of it being sequestered as dense sulfates, with the potential for self-healing. Experimental results obtained by Razak et al. (2024) also indicate that the presence of H_2S in dissolved CO_2 brine has the potential to reduce the dissolution of carbonate rocks. All of these studies highlight the impacts of these impurities on carbonate reservoirs. However, there are still significant research gaps concerning the broader implications of these impurities on CO_2 sequestration in carbonate reservoirs under varying reservoir conditions, especially on a field scale. More experimental and numerical studies at the field scale are needed to fully understand the implications of these impurities on the long-term stability and effectiveness of CO_2 storage in carbonate reservoirs.

3.6. Wellbore-reservoir injection

The injection of CO_2 in carbonate formations could potentially trigger a series of interconnected effects, including changes in injectivity. Injectivity is complex, arising from the interaction of several parameters, including rock fabric, fluid composition, thermodynamic conditions, and flow regime (Egermann et al., 2005). Furthermore, changes in near-wellbore porosity and permeability due to water vaporization, fines migration, salt precipitation, and CO_2 hydrate formation also affect the injectivity of CO_2 (Ahamed et al., 2021; Barbosa Machado et al., 2023a; Gauteplass et al., 2020; Yusof et al., 2022). For successful CCS projects in carbonate reservoirs to proceed, understanding geochemical reactions around the wellbore is critical because the flow field is highly heterogeneous, and CO_2 injections strongly perturb the initial geochemical equilibrium in this region (André et al., 2007). At early times, due to high injection rates and pressures, viscous forces dominate CO_2 flow as dry-out begins to develop; some water backflow is expected near the injector, driven by capillary forces, which also dominate at late times and far-field in addition to buoyancy forces (Fernandes et al., 2024; Krishnamurthy et al., 2022). In carbonate formations, strong calcite dissolution increases injectivity around the well bore and decreases the capillary snap-off of the CO_2, which would lead to a decrease in the residual trapping potential around the wellbore in granular carbonate formations (Seyyedi et al., 2020). This acid dissolution, governed by acid mass transfer kinetics, exhibits a strong dependence on flow rate (Egermann et al., 2005; Xie et al., 2023). From the perspective of injectivity, carbonate dissolution may appear favorable; however, it can weaken the rock strength, induce reservoir compaction, and raise long-term integrity concerns (Raza et al., 2020). On the other hand, CO_2 injection in carbonate formations could result in reduced injectivity of the well, due to changes in the multiphase flow relative permeability as well as the mineral precipitation (Mohamed and

Table 2
Reactive transport studies of CO_2 sequestration in carbonate rocks.

Author(s)	Objectives	Methodology	Key Findings
(Amin and Azuddin, 2016)	Study the long-term geochemical effects of CO_2 injection into a carbonate field with natural CO_2 accumulation. Also studied salt precipitation as well as impact on porosity from dissolution and precipitation.	2D homogeneous radially symmetric reactive transport model with TOUGHREACT, at 352 bars and 140 °C. Injection via a horizontal well below gas water contact (GWC). 300 years of simulation (including 30 years injection).	Minimal geochemical alteration of injection CO_2 into solid phase, due to initial high CO_2 saturation in aquifer. Alterations are confined to below GWC. Largest dissolution and precipitation of primary carbonates in areas of highest pH (injected plume and plume edges). Minor salt precipitation due to formation dry-out around injector. No major impact on injectivity.
(André et al., 2007)	Evaluate the evolution of CO_2-induced geochemical reactivity in space and time.	1-D radial model with TOUGHREACT. Injection of $scCO_2$ and CO_2-saturated water at 75 °C. 0.3 million tonnes of CO_2 injected for 10 years.	Higher reactivity with CO_2-saturated solution (90 % porosity increase around wellbore). Non-reactivity and lower geochemical reaction with scCO2 (5–7 % global porosity increase) Mineral precipitation and liquid vaporization around wellbore. Porosity evolution with distance from injector depends on carbonate dissolution and mineral scaling.
(Azuddin et al., 2019b)	Study the impact of temperature on CO_2-induced mineral reaction	Core flood experiments using acidified brine in a limestone core, at temperatures ranging from 21 °C to 70 °C and reactive transport modelling using CMG-GEM. Model calibration with experimental data followed by temperature and flow rate sensitivity.	Ca^{2+} and Mg^{2+} released decrease with increase in flow rate at all temperatures. Degree of dissolution also higher at lower flow rate due to higher residence times. (NB: equilibrium was not reached in the experiment). Porosity decreases then increase while permeability increases with increase in temperature. Higher calcite dissolution than dolomite, more at higher temperature. Elevated dissolution near wellbore.
(Fu et al., 2015)	Investigate rock dissolution during convective mixing and analyze the impact of geochemical reaction on mass exchange rate. Examine the interaction between fluid flow and chemical reactions driven by permeability alterations caused by rock dissolution.	Adopted a mixing-limited reactive transport system assuming instantaneous chemical equilibrium, hence completely decoupling transport from reaction; the local reaction rate thus being described based on scalar dissipation and chemical speciation. Employed high-resolution 2D and 3D simulations domain composed primarily of calcite	Dissolution starts in high mixing zones but stops earlier than convective mixing due to nonlinear chemical behavior. Rock dissolution and increase in porosity occurs primarily near the top boundary, significantly enhancing fluid mixing and solubility rates, potentially improving CO_2 trapping efficiency in migrating plumes. Below the boundary layer, permeability changes are minor, causing limited influence on convective fingering dynamics.
(Iloejesi et al., 2024)	Investigate the impact of temperature, carbonate mineral and porosity heterogeneity on CO_2 trapping efficiency.	TOUGHREACT and ECO2 N EOS module. 2D radially symmetric model with constant pressure boundaries Homogeneous vs heterogeneous model with spatial variation of carbonate mineral fraction. 10-year injection and 40-year post-injection.	During the injection phase, heterogeneous petrophysical properties and carbonate mineral distribution show higher CO_2 trapping compared to homogeneous domains (10 % deviation was observed). Post injection, homogeneous model result in higher CO_2 trapping. Including vertical temperature gradient within a model domain also results in higher CO_2 trapping, compared a uniform temperature domain, due to higher reaction kinetics at the deeper injection zone.
(Li et al., 2024)	Evaluate the impact of mineral dissolution and precipitation on the spatio-temporal evolution of porosity and permeability in a depleted fractured carbonate reservoir.	Fully couple 3D THMC model using FALC3D-TOUGHREACT. 10-year injection at 0.1kg/s and 50-year post-injection period in a formation comprising predominantly calcite (38 %) and dolomite (47 %)	Inhibited geochemical reaction around the wellbore due to high CO_2 concentration. More reactivity observed at about 200 m from wellbore. Predominant dissolution reaction for first 5 years – increase in porosity & permeability, followed by decrease due to mineral precipitation. Minimal impact on under/overlying strata. Enhanced caprock stability, and sealing properties due to secondary mineral precipitation at reservoir-caprock boundary
(Tambach et al., 2017)	Study the long-term behaviour of CO_2 in carbonate aquifer including geochemical stability, plume migration, influence of model realization and well location	Coupled fluid flow using MoReS & geochemistry with PHREEQC. Target formation predominantly calcite with some dolomite minerals. 1000 years of simulation including 30 years of injection.	Relatively low geochemical impact of CO_2 injection into carbonate aquifer. Dissolved or precipitated minerals are negligible with only about 0.03 % increase in porosity after 1000 years. Significant reduction of pH in the CO_2 plume. Outside the CO_2 plume area, mineral reactions (though relatively small) also take place as a result of the increase in pressure from CO_2 injection.
(Xie et al., 2023)	Investigate calcite dissolution near the wellbore, via pore scale numerical method	Pore-scale numerical model using the lattice Boltzmann method to simulate the combined effects of heterogeneous reactions, mass transport and fluid flow on the evolution of calcite structures. Single phase multi-component/mineral reactive transport model. Various flow rates and temperatures investigated.	High pressure (advection dominated) can lead to calcite dissolution far from inlet due to more contact with fresh carbonate acid, however with increasing undissolved calcite fraction. The influence of ΔP on calcite dissolution reduces with higher temperature. Poor reaction rate at low temperature can be compensated for by higher flow rate. High ΔP result in heterogeneous dissolution.

Nasr-El-Din, 2012). In addition to precipitation, there is fine migration, pore blockage from agglomeration of minerals and salt precipitation due to brine desiccation; these effects may cause fluid pressure near the well bore to increase, leading to borehole breakdown effects. André et al. (2007), in their numerical simulation, observed brine desiccation results in the precipitation of dolomite, anhydrite, and some calcite, leading to a porosity decrease from 10 % to 1 % around the wellbore.

Controlling the injection pressure and rate is important for effective CO_2 storage in carbonate rocks. Generally, low permeability rocks with high capillary entry pressures are less suitable for CO_2 storage reservoirs because of high injection rates, which may be required to overcome the high capillary entry pressure, hence leading to possible induced formation fracturing (Mohamed and Nasr-El-Din, 2012). Higher injection pressures and rates at the wellbore result in a high Peclet number and low Damköhler number which in turn favors advection-dominated transport and potentially increasing rock dissolution in the nearfield, stimulating the growth of a very localized dissolution with the occurrence of highly conductive wormholes, thereby promoting injectivity (Randi et al., 2017). For advection-dominated flow, initiation of uniform dissolution is less probable (Randi et al., 2017). In their experimental study, Izgec et al. (2008) observed the completion of chemical reactions at lower injection rates leading to increased precipitation rates and chances of plugging the pore throats located around the beginning of the flow path. However, their observations indicated that the salt concentration of the brine has a more pronounced impact on reducing permeability compared to the flow rate. Prevention of re-precipitation could also be achieved by faster flow rates, which ensures that the contact between the surface of the rock and CO_2 is continuously maintained (Eyinla et al., 2023). Moreover, intermittent injection generates higher flow heterogeneity and dispersion, encouraging enhanced dissolution of CO_2 into saline water (Kovacs et al., 2015). Summarily, the optimal injection rate, well type, and location in the reservoir will depend on the specific reservoir characteristics and the desired outcomes of the injection process. While slow injection rates may facilitate the completion of chemical reactions, promoting precipitation rates and plugging of pore throats, high injection rates with shorter fluid residence times may lead to rock dissolution and injectivity enhancement.

3.7. *Injection induced geo-mechanical changes*

The compaction failure caused by rock degradation upon exposure to CO_2-rich brine, as well as the buildup of pore pressure, are two competing mechanisms contributing to rock failure in deep carbonate formations during CO_2 sequestration (Zhou, 2011). Injection of $scCO_2$ and live brine (CO_2-saturated brine) experiments conducted by Zhang et al. (2018) in limestone rock samples at reservoir conditions showed a decrease in Young's modulus in both cases; however, live brine (CO_2-saturated brine) results in higher decrease compared to $scCO_2$. They also observed a slight drop in Poisson's ratio after $scCO_2$ and an increase with live brine, suggesting that Poisson's ratio can be used for monitoring carbonate dissolution, which further implies that geophysical methods may be effective for assessing carbonate dissolution at field scale. Similarly, experimental studies conducted by Raza et al. (2020) in limestone core samples showed that post-CO_2 injection, dynamic bulk modulus (measured with an ultrasonic pulse) and static bulk modulus (from unconfined compression test) reduced by 20 % and 52 %, respectively. Consequently, limestone compressibility, the inverse of bulk modulus, will increase with a high tendency for compaction during the injection and post-injection phase (Raza et al., 2020). Renard et al. (2005) found a significant increase in the rate of carbonate matrix compaction by a factor of 50–70 due to elevated partial pressure of dissolved CO_2 of up to 30 MPa. Al-Ameri et al. (2015) observed a 500 ft thick Khuff limestone carbonate formation compacting by 1.25 ft due to CO_2 sequestration for 90 days, as well as a decrease in compressional wave velocity, Poisson's ratio, and Young's modulus in other carbonate rock samples (Fig. 6). Al-Dhafeeri et al. (2023) observed that higher confining pressure results in a lower reduction of rock strength due to pore space and wormhole compression.

Thermal effects also play a role in rock geo-mechanical changes. Injecting CO_2, which is typically colder than the reservoir rock, cools further during expansion, impacting the geo-mechanical properties of carbonate rocks. In their modeling studies, Goodarzi et al. (2015) found that depending on injection rates, thermal effects from the injection could lower the injection capacity and avoiding formation of induced fractures may prove to be impractical. They observed that cooling of formation from CO_2 injection reduces the total stresses, lowering the fracture propagation pressure, which in turn reduces the pressure window available for injection and decreases injectivity. Experiments

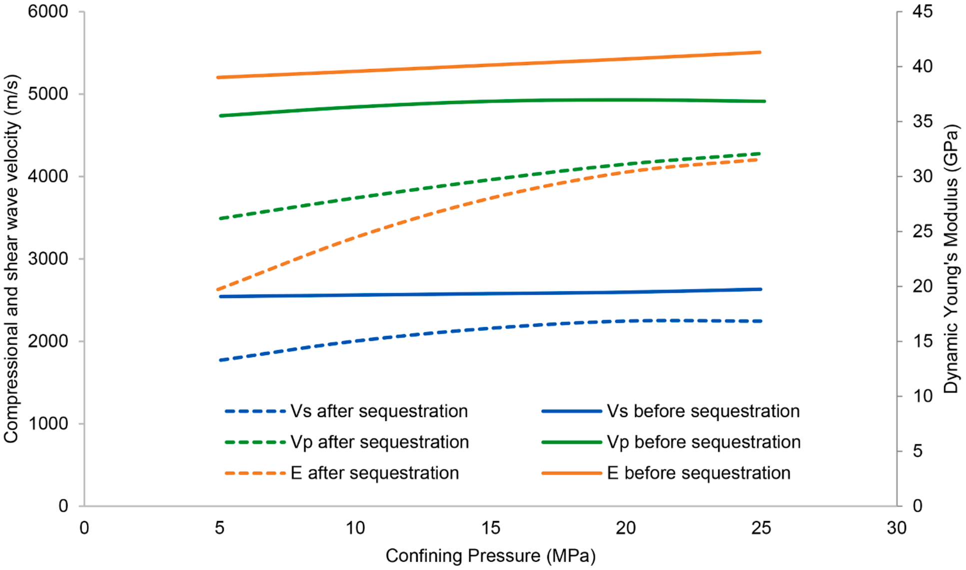

Fig. 6. Comparison of compressional wave velocity (V_p), shear wave velocity (V_s), Young's modulus (E), and Poisson's ratio (ν) of Indiana Limestone before and after 90 days of CO_2 sequestration, modified after AL-Ameri et al. (2015). The results indicate a significant decrease in seismic velocities and Young's modulus after sequestration, particularly at lower confining pressures.

conducted by Al-Dhafeeri et al. (2023) at various temperatures (35, 60, 85 °C) showed that the highest reduction in Young's modulus occurs at 85 °C. This was because at higher temperature, CO_2 solubility is lower (as discussed in Section 3.3) which resulted in slower reaction and increased contact time between the carbonated CO_2 and rock sample.

The geo-mechanical changes experienced by carbonate rocks also depend on the mineral composition. Carbonate rocks with reduced carbonate mineral content may not be as susceptible to reduction in mechanical strength, as the presence of the non-carbonate minerals acts as buffer, reducing the reactivity (Eyinla et al., 2023). It is also important to note that pore blockage from mineral precipitation in carbonates may also offset the dissolution-induced rock porosity, which may lead to reduced chances of rock failure (Raza et al., 2020). Also, the reactivity of $scCO_2$ is substantially lower than CO_2-saturated water (André et al., 2007). Hence, the geo-mechanical changes observed in some laboratory experiments with acidified brine may be relatively higher. The implication of these geo-mechanical changes on reservoir full-field monitoring in carbonate needs further investigation to develop tools for better monitoring, especially in the vicinity of the wellbore where higher dissolution takes place. The high reactivity, heterogeneity, and complexities in the microstructures of carbonates pose challenges in applying traditional seismic monitoring techniques of CO_2 in carbonate reservoirs (Ghosh and Sen, 2020; Rasheed Adebayo et al., 2014). The associated change in rock acoustic properties (P-and S-wave) due to rock dissolution can play a key role in monitoring. A study on the impact of effective stress on wave velocities in a depleted carbonate reef in the Michigan Basin by Raziperchikolaee et al. (2022), indicate that the alterations in saturation and effective stress both affect the velocity changes in the reservoir. Hence, incorporating the poro-elastic effect of stress on changes in velocity improves the interpretation of seismic attributes during CO_2 injection in carbonate reservoirs. Ghosh & Sen (2020) proposed a pressure differential effective medium (PDEM) theory that aids in 4D seismic data analysis by detecting velocity changes, variations in the elastic properties of carbonate reservoirs saturated with CO_2, as well as monitoring of CO_2 movement while also addressing micro to meso-scale fractures and chemo-mechanical effects. Their findings reveal that the combined effect of rock dissolution and free CO_2 saturation on rock velocities is an indication that both attenuation and dispersion reduce as the saturation shifts from water to gas.

4. Case studies and field trials

4.1. Hontomin project (Compostilla OXY-CFB-300 project)

The Hontomin pilot project, Spain, represents a one of the few global geological CO_2 storage projects in a carbonate saline aquifer. The objective of this research project was to enhance the understanding of CO_2 injection in low permeability fractured carbonates, including physio-chemical processes, testing and monitoring techniques, and to establish safe and efficient operational criteria for transitioning from pilot scale to industrial scale (Alcalde et al., 2014). The geologic setting is a dome-like structure with a fractured reservoir of lower Jurassic Sopeña limestone and dolomite, with marl as top seal and anhydrite as bottom seal (Kovacs et al., 2015; Sohal et al., 2021) The limestone reservoir is 79 m thick at a depth of 1435 m, while the dolomite layer is 41 m thick at a depth of 1514 m (Sohal et al., 2021). The reservoir is characterized by low matrix permeability and porosity, dominated by a network of fractures (de Dios and Martínez, 2019). One injector and one monitoring well, 50 m apart, were drilled to perform a series of tests on the site. Permeability was measured in the injector and monitoring wells, ranging from 1.5×10^{-17} m^2 to $1.9 \times 10^{-15} m^2$ (0.015 to 1.9 mD) (Kovacs et al., 2015). During the testing phase, 14,000 m^3 of brine and 2300 cumulative tons of CO_2 were injected to quantify initial field-scale permeability, confirm hydraulic connectivity between wells, and determine reservoir and caprock fracture pressure (de Dios et al., 2017). The following observations were noted during the testing phase: (1) Brine injection conducted with a pressure exceeding the reservoir leak-off test value by 0.5–1 MPa (5–10 bar) showed that the overpressure did not affect seal integrity; however, it did produce micro-seismic effects, with the degree of magnitude correlating with the injection-induced hydrodynamic effects. (2) Brine injections improved injectivity, likely due to hydrodynamic effects, such as fracture dilation, in the fracture network. Co-injecting CO_2 and brine further increased permeability, potentially due to geochemical effects, such as rock dissolution and transport. At the end of the hydraulic characterization, the reservoir permeability increased from 4.9×10^{-16} m^2 (0.5 mD) during the drilling phase to 1.5×10^{-14} m^2 (15 mD) due to the combined hydraulic, chemical, and mechanical changes in the target reservoir (de Dios et al., 2017). These results offer compelling field-scale evidence that coupled feedback between physical and chemical processes will play a fundamental role in the development of industrial CCS operations in carbonate reservoirs.

4.2. American electric power (AEP) mountaineer CCS project

The aim of the AEP Mountaineer project in New Haven, West Virginia, USA, was to determine the technical feasibility of deep saline aquifer sequestration of CO_2 captured onsite from a coal-fired power plant (Gupta et al., 2008). The project comprised two injection wells, AEP-1 and AEP-2, respectively, targeting the Copper Ridge dolomite at approximately 2500 m depth and the Rose Run sandstone at 2350 m depth, and three deep observation wells (Gupta et al., 2013). The Copper Ridge injection zone featured vuggy intervals characterized by high porosity and permeability in contrast with the Rose Run injection zone consisting of thin, interlayered sandstone and dolomite zones (Mishra et al., 2013). Overlying the Rose Run formation is the Beekmantown dolomite seal (185 m thick), while the Nolichucky shale (30m thick) underlies the Copper Ridge dolomite. No faults were identified from the seismic survey with the closest regional fault about 25 miles to the southeast of the plant (DOE, 2011). Injection commenced in October 2009 ending in May 2011 after achieving the injection validation target (McNeil et al., 2014). About 10,000 metric tons and 27,000 metric tons of CO_2 were injected into the sandstone and dolomite formations, respectively (Mishra et al., 2013). Post-injection analysis by McNeil et al. (2014) and Mishra et al. (2014) indicates the following: (1) Pressure response was different in the two formations, with the Rose Run sandstone experiencing a larger pressure increase (several hundred psi) and a longer fall-off time back to pre-injection levels, than the Copper Ridge dolomite (<100 psi). This difference was consistent with the estimated permeability values of the two formations – lower permeability in the sandstone and higher in carbonate. Pressure stabilization occurs after about 1000 days in the carbonate reservoir, monitored from an observation well 670 m away. (2) Well-calibrated reservoir model with field data predicts plume extent between 925 and 975 ft (281–287 m) for the Copper Ridge dolomite formation and between 460 and 510 ft (140–155 m) in the Rose Run formation. The plume stabilizes after about 600 days for both formations.

Other pilot projects include the Shenhua Group CCS Demonstration project, China's first deep saline aquifer storage project, that injected a total of 0.302 million tonnes of CO_2 between 2011 and 2014 into a tight carbonate reservoir using hydraulic fracturing to enhance secondary porosity (Baines et al., 2020). The Lacq-Rousse project in France was designed to store CO_2 in the depleted Rousse Mano dolomitic gas reservoir at a depth of 4200 m, where the reservoir is overlain by a thick series of marls, shales, and silts (Lescanne et al., 2011; Thibeau et al., 2013). Between 2009 and 2013, ~51,000 tonnes of CO_2 was injected with no leakage detected (Albertz et al., 2022). Moreover, seismic monitoring at the Lacq-Rousse project recorded very low seismic activity during the first two and half years, suggesting that injection pressure did not adversely affect the geo-mechanical integrity of the storage system (Prinet et al., 2013)

While there have only been a small number of pilot projects for carbon sequestration in carbonate reservoirs, the AEP Mountaineer, Hontomin, Shenhua, and Lacq-Rousse projects all successfully demonstrated the high potential these geologic formations hold for storing CO_2. The demonstration projects targeting high primary permeability and porosity reservoirs, i.e., the Mountaineer and Lacq-Rousse projects, were capable of storing thousands to hundreds of thousands of tonnes of injected CO_2 with minimal induced seismicity and pressure buildup-related risks. Furthermore, the Hontomin and Shenhua projects demonstrated how, even in tight carbonate reservoirs, engineered systems, e.g., hydraulic fracturing, can improve the secondary porosity and permeability, allowing these reservoirs to hold kilotons of CO_2. We note that to date, no CCS projects have attempted to store millions of tons of CO_2 in carbonate reservoirs; however, several projects have been announced to assess the potential for megaton storage hubs in carbonate reservoirs in Florida. The CarbonSAFE Phase III TECO Project and the CarbonSAFE Phase II Project ACCESS are both investigating the feasibility of sequestering at least 50 million tons of CO_2 at sites near Tampa Bay and Miami, respectively. These newly announced projects in the United States will seek to build on the previous kiloton carbonate storage demonstration projects by establishing the first megaton carbonate storage facilities. In summary, past demonstration projects have demonstrated that both permeable and tight carbonate formations are capable of kiloton geologic carbon sequestration, and future studies are working to establish the feasibility of megaton carbonate formation storage.

5. Summary and general recommendations

The prevalence of carbonate rocks in most sedimentary basins and proximity to CO_2 sources, makes them a valuable resource for geologic CO_2 storage. The few pilot and experimental projects conducted globally offer insights into the viability of GCS in carbonate reservoirs. Nonetheless, the complexity of carbonates and high mineral reactivity poses a challenge. While carbonate minerals exhibit reactivity with carbonated brine, the consequent dissolution that follows the injection of CO_2 may not always be detrimental. Specifically, carbonate dissolution buffers pH levels in the reservoir to counter excessive dissolution and potentially promote mineral trapping, particularly when flow rates decrease and fluid residence time increases, e.g., at the leading edge of the advancing CO_2 plume and/or during post-injection plume stabilization. Nevertheless, the extent of mineral trapping in carbonate formations remains a source of uncertainty that requires additional bench- and field-scale research to fully understand. Despite this uncertainty, however, other trapping mechanisms, such as structural, solubility, and residual trapping, contribute substantially to the overall storage capacity of carbonate formations. While small-scale lab experiments provide valuable insights into the behavior of carbonates in contact with CO_2, it is relevant to consider field-scale processes if carbonate CCS is to become a part of the carbon management portfolio. For example, the effects of mineral precipitation in carbonates may reduce porosity and permeability by plugging pores. This process may counteract the effects of the dissolution-induced porosity increase and potentially reduce the risk of rock failure on a global level. These effects will strongly influence the performance characteristics of CO_2 storage in carbonate reservoirs, and substantially more research is needed to guide the development of industrial-scale CCS in carbonates. Our review also finds that petrophysical heterogeneity in carbonates can either aid CO_2 storage by plume dispersion or lead to CO_2-front non-conformance by excessive channeling through zones of high permeability. This is in addition to potential wormhole formation that impacts CO_2 migration, storage efficiency, and mechanical integrity. Increasing the ability to characterize physical and mineralogical heterogeneity at field-scales is a frontier area of research, and substantial advances are needed in this area to gain deeper insights into the effects of heterogeneity on CO_2 trapping mechanisms in carbonate reservoirs. The meso-scale shale/clay layers and lithological heterogeneity in reservoirs, like those observed in the Sleipner project, can affect CO_2 plume behavior and storage capacity. Understanding these complexities requires advanced seismic techniques and detailed core analysis for accurate assessment and long-term planning. In addition, special attention must be given to near-wellbore integrity effects during injection, as chemical reactions, rock dissolution and potential mechanical instability are more prevalent in this region, and may lead to deleterious effects, such as well-clogging, pressure accumulation, and wellbore breakdown. In addition, routine and special post-injection monitoring techniques need to be developed to monitor rock, CO_2 plume and pressure behavior in carbonate reservoirs.

Building on the preceding discussions regarding the feasibility and potential effectiveness of carbon capture and storage carbonate formations, the following general recommendations are given.

1. Carbonate reservoirs overlain by non-reactive/non-carbonate seals are recommended to prevent cap rock dissolution, the result of which will compromise the seal integrity and overall containment. The presence of petrophysical heterogeneity, common in carbonates slows down CO_2 migration to the top of structure/gas cap, further preventing excess reactivity within seals or caprock. Carbonates with fewer natural fractures are favorable, as they minimize the risk of fracture aperture erosion and growth from carbonic acid-rock reaction, which could potentially compromise containment. Within this context, detailed petrophysical characterization to understand the spatial distribution and genetic mechanisms that result in meter-scale reservoir heterogeneity will be an important factor in developing successful carbon storage sites in carbonate-hosted reservoir systems.
2. From the standpoint of avoiding excessive rock dissolution, carbonate formations with dolomite are recommended since they have a lower rate of dissolution than calcite. Dolostones are more resistant to the porosity/permeability-reduction process (Amthor et al., 1994); hence, dissolution tends to result in a slower porosity/permeability evolution due to lower reactivity compared to limestone (Hao et al., 2015). However, in terms of mineralization, calcite minerals may result in relatively higher mineral trapping, albeit at very low rates and at an extremely long time period, as indicated by several reactive transport studies.
3. To reduce susceptibility to CO_2-induced mechanical weakening, consideration should be given to CO_2 injection into “impure” carbonate rocks with non-carbonate minerals (e.g. silicates), as the buffering effect of non-carbonate minerals can limit CO_2-carbonate mineral reactions (Eyinla et al., 2023).
4. Preferred optimal storage conditions include injection into dolomite or magnesite-rich carbonates far from the injection point, presence of calcite near the wellbore, 100–150 °C temperatures, and CO_2 partial pressure exceeding 50 bars (5MPa) (Pokrovsky et al., 2009)
5. A crucial aspect of the successful implementation of CCS projects in carbonate reservoirs is the comprehensive understanding of geochemical reactions occurring around the wellbore. This is essential due to the highly heterogeneous flow field and significant perturbations to the initial geochemical equilibrium induced by CO_2 injections, especially around the wellbore (André et al., 2007). Higher flow rates reduce mineral precipitation but increase rock dissolution. On the other hand, low flow rates pose the risk of pore blockage from mineral precipitation.

6. Recommendations: further research

The impact of commonly found impurities in CO_2 stream (e.g. sulphur compounds, nitrogen oxides, etc.) on the dissolution and precipitation kinetics in carbonate reservoirs warrants further investigation because these processes affect the reaction pathways, geo-mechanics, and potential storage efficiency. We re-echo the need highlighted by Xu et al. (2011), for detailed mineralogical assessment of rocks, refinement of thermodynamic properties at high temperatures and pressures, and reliable reaction rates of mineral dissolution/precipitation at field scale for better quantitative prediction of geochemical evolution and long-term mineral trapping.

Understanding the evolution of the kinetics and dynamics of these CO_2 reactions in carbonate reservoirs in both the near and far-fields is paramount. In the near field, rapid acidification and dissolution may prevail, influencing the initial storage conditions. As the flow rate slows down post-injection and more reservoir volume is accessed, the pressure of carbonated brine decreases, and pH levels tend to increase, triggering re-precipitation reactions of carbonate minerals. This shift from dissolution to re-precipitation can have a profound impact on the long-term stability of the stored CO_2. The speed of reaction, acidification, and dissolution processes directly impact the storage capacity of carbonate reservoirs for CO_2 sequestration. To optimize storage capacity and mechanisms, it is essential to study how these kinetics and dynamic changes both experimentally and numerically. Quantification of the evolution of petrophysical properties and the ability to monitor the progress of reaction rates with geophysical methods, at field scale in carbonate reservoirs is also paramount. The recently announced Department of Energy (DOE) CarbonSAFE projects in carbonate formations serve as catalysts for advancing this endeavor to expedite the development and implementation of efficient CCS strategies in carbonate reservoirs, contributing significantly to carbon mitigation efforts and fostering sustainable energy practices.

Most numerical studies model carbonate reservoirs with uniform petrophysical properties. However, the geology of carbonate is complex, and actual field results may differ significantly from such simplified models. Studies should be conducted to capture the multiscale sedimentary and stratigraphic heterogeneities and other complexities of carbonate reservoirs through rigorous reservoir characterization. Such models with multiple geologic realizations will help evaluate the impact on storage security and various storage efficiencies while quantifying uncertainty. Also, the influence of carbonate reservoir heterogeneity on relative permeability hysteresis and consequent impact on residual trapping, especially in saline aquifers, requires further investigation, both experimentally and numerically.

There are also limited Thermo-Hydro-Mechanical-Chemical (THMC) coupled models in carbonate reservoirs CO_2 storage. Such models will improve the prediction of CO_2 plume migration and trapping, enhance understanding of carbonate geomechanics, aid optimization of injection strategies, including optimal well location, and evaluate long-term storage security. It is obvious that structural deformation occurs in carbonate reservoirs during storage; however, the level of structural deformation that is acceptable requires more investigation. Further studies are required to test various injection rates in carbonate reservoirs, including the use of horizontal wells, which could increase CO_2 dissolution due to high reservoir contact and the impact of perforation location on storage efficiencies.

Disclaimer

This material is based on work supported by the Department of Energy under award number DE-FE0032447 through the Southeast Regional Carbon Sequestration Partnership (SECARB), which is managed by the Southern States Energy Board under contract number SSEB-SECARBUSA-931-VAT-2020. This manuscript was prepared as an account of work sponsored by an agency of the U.S. government. Neither the U.S. government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. government or any agency thereof.

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Uzezi D. Orivri: Writing – review & editing, Writing – original draft, Visualization, Resources, Project administration, Methodology, Investigation, Data curation, Conceptualization. **Piyali Chanda:** Writing – review & editing, Writing – original draft, Visualization, Resources. **Liz Johnson:** Resources, Data curation. **Lars W. Koehn:** Writing – review & editing, Visualization, Software, Resources. **Ryan M. Pollyea:** Writing – review & editing, Supervision, Project administration, Methodology, Funding acquisition.

Declaration of competing interest

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

Ryan M. Pollyea reports financial support was provided by Department of Energy under award number DE-FE0032447 through the Southeast Regional Carbon Sequestration Partnership (SECARB), which is managed by the Southern States Energy Board under contract number SSEB-SECARBUSA-931-VAT-2020. 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.

Acknowledgements

The authors express gratitude to the Editor, Associate Editor, and Reviewers of the *International Journal of Greenhouse Gas Control* for dedicating time in reviewing and accepting this article.

Data availability

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

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