energies

Review

Geochemistry in Geological CO_2 Sequestration: A Comprehensive Review

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Abstract: The increasing level of anthropogenic CO_2 in the atmosphere has made it imperative to investigate an efficient method for carbon sequestration. Geological carbon sequestration presents a viable path to mitigate greenhouse gas emissions by sequestering the captured CO_2 deep underground in rock formations to store it permanently. Geochemistry, as the cornerstone of geological CO_2 sequestration (GCS), plays an indispensable role. Therefore, it is not just timely but also urgent to undertake a comprehensive review of studies conducted in this area, articulate gaps and findings, and give directions for future research areas. This paper reviews geochemistry in terms of the sequestration of CO_2 in geological formations, addressing mechanisms of trapping, challenges, and ways of mitigating challenges in trapping mechanisms; mineralization and methods of accelerating mineralization; and the interaction between rock, brine, and CO_2 for the long-term containment and storage of CO_2. Mixing CO_2 with brine before or during injection, using microbes, selecting sedimentary reservoirs with reactive minerals, co-injection of carbonate anhydrase, and enhancing the surface area of reactive minerals are some of the mechanisms used to enhance mineral trapping in GCS applications. This review also addresses the potential challenges and opportunities associated with geological CO_2 storage. Challenges include caprock integrity, understanding the lasting effects of storing CO_2 on geological formations, developing reliable models for monitoring CO_2–brine–rock interactions, CO_2 impurities, and addressing public concerns about safety and environmental impacts. Conversely, opportunities in the sequestration of CO_2 lie in the vast potential for storing CO_2 in geological formations like depleted oil and gas reservoirs, saline aquifers, coal seams, and enhanced oil recovery (EOR) sites. Opportunities include improved geochemical trapping of CO_2, optimized storage capacity, improved sealing integrity, managed wellbore leakage risk, and use of sealant materials to reduce leakage risk. Furthermore, the potential impact of advancements in geochemical research, understanding geochemical reactions, addressing the challenges, and leveraging the opportunities in GCS are crucial for achieving sustainable carbon mitigation and combating global warming effectively.

Keywords: geochemistry; geological carbon sequestration; CO_2–brine–rock interactions; CO_2 trapping

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Citation: Fentaw, J.W.; Emadi, H.; Hussain, A.; Fernandez, D.M.; Thiyagarajan, S.R. Geochemistry in Geological CO_2 Sequestration: A Comprehensive Review. *Energies* **2024**, *17*, 5000. https://doi.org/10.3390/en17195000

Academic Editor: Renato Somma

Received: 1 September 2024
Revised: 28 September 2024
Accepted: 2 October 2024
Published: 8 October 2024

1. Introduction

According to our world in data, in 2022, over 35 billion tons of CO_2 were emitted from fossil fuels and industries throughout the year. Emitted CO_2 can persist in the atmosphere for an extended period, thereby perpetuating its influence on global warming long after its initial release [1]. This emission of anthropogenic CO_2 has significantly contributed to global climate change, which impacts the Earth's ecosystem [2,3]. The Paris Agreement, reached by 197 countries, aims to restrict the Earth's average temperature rise to 1.5 °C [4]. The International Energy Agency (EIA) forecasts that 2.3 gigatons of CO_2 will be stored annually by 2060 in order to meet the IPCC (Intergovernmental Panel on Climate Change)-60 climate target [5]. To meet this outlined climate target, the global carbon capture capacity of approximately 40 million tons of CO_2 per year has to be scaled up significantly, and by 2050, it must be increased to over 5600 million tons per year (MtpaCO_2) if countries intend to restrict global warming to 2 °C [6,7]. One of the main challenges in increasing this capacity is storing large volumes of CO_2 [8].

Storing is the final step for the carbon capture and storage (CCS) process, which comes after capturing and transporting. Capturing is the process of separating CO_2 emissions or pure CO_2 streams from other gases released from industrial facilities or factories before entering the atmosphere. The CO_2 then undergoes compression and transportation to a storage location and is injected deep underground into selected geological formations, where it is intended to be securely stored for long-term isolation from the atmosphere [7,9–11].

The storing process also involves post-injection monitoring to permanently store CO_2 and prevent its release back into the atmosphere. There are various ways to store CO_2 in different forms and locations. The most common types of CO_2 storage are ocean storage, mineralization, chemical conversion, and geological storage. From these carbon storage types, geological carbon sequestration (GCS) is the only feasible method to store large volumes of CO_2 [8]. It is an effective approach for reducing greenhouse gas (GHG) emissions by reducing anthropogenic CO_2 emissions and, hence, reducing global warming regardless of implementing clean and efficient energy solutions [12–14].

Types of geological storage include saline formations, depleted oil and gas fields, using CO_2-EOR, deep unmineable coal seams, and in situ and ex situ carbon mineralization (Albertz, Stewart, and Goteti, 2022 [15–17]). Sequestration in saline aquifers is the most mature storage technique of all the geological storage types. The primary reason for this is that saline aquifers have the largest volumetric potential for geological CO_2 storage [13,15]. Garcia, Kaminska, and Maroto-Valer, in 2010 [18,19], indicated that saline aquifers have a capacity to store 10,000 gigatons of CO_2. Other reasons include them not being suitable for supplying potable water because they are highly mineralized, and they have suitable porosity and permeability [20].

Storage of CO_2 in geological formations heavily depends on the two intricately linked aspects, geomechanics and geochemistry, to ensure the safe, prolonged subsurface storing of the gas. These two processes are always coupled in geological storage. Geomechanical aspects focus on the physical and mechanical behavior of the subsurface formations where the CO_2 is injected and stored, while the geochemical or geochemistry aspects pertain to the chemical reactions of the injected CO_2, the host rock, and the formation fluids. Table 1 depicts the difference between the geochemical and geomechanical aspects in geological processes.

Table 1. Geochemical and geomechanical aspects in geological analysis.

Geomechanical Aspects	Geochemistry/Geochemical Aspects
• Rock strength and integrity	• Dissolution of minerals/supercritical CO_2
• Induced seismicity	• Precipitation of minerals
• Petrophysical properties (porosity and permeability or rock injectivity)	• Mineralization
	• Geochemical reactions
• Stress changes	• Plume migration

In geological storage, the injected CO_2 will have different fates when it comes into contact with the host rock and the formation fluids. A portion of the injected CO_2 fills the pore space within the storage site, which is called structural or stratigraphic trapping; some dissolves in water, which is known as solubility trapping; some is trapped as residual CO_2 by capillary forces; and some of it may form carbonate minerals through precipitation or mineral trapping [21]. These four principal trapping mechanisms have distinctive contributions to immobilizing CO_2 for effective geological carbon sequestration. The trapping can happen immediately after CO_2 injection or over hundreds of years based on factors like CO_2 dissolution in the formation fluid and the dissolution of rock and precipitation of rock minerals [22]. Furthermore, the CO_2–brine interaction in GCS applications can either significantly enhance or compromise the caprock seal integrity over time, which, in turn, is the main factor affecting the leakage of CO_2 [23].

Thus, since injecting CO_2 into the subsurface region alters the chemical equilibrium of the system, causing the dissolution/precipitation of minerals and subsequently changing the rocks' petrophysical properties, a comprehensive understanding of the geochemistry of the system is essential to guarantee sufficient, secure, and efficient storage of CO_2 [24].

There are still research demands and scientific gaps in this aspect, especially in terms of a comprehensive understanding of the interaction between CO_2, brine, and rock, the effects of temperature, pressure, and salinity on CO_2 wettability in GCS conditions, and the mechanisms by which CO_2 is mineralized in different formations [25–29]. Conversely, GCS depends highly on petrophysical parameters, including interfacial tension between the rock and fluid, the wettability of the rock–CO_2–brine system, irreducible fluid saturation, and the pore porosity and permeability [30–32].

Thus, a comprehensive review of studies carried out so far in geochemistry is crucial to articulate the gaps and findings and give directions for future research. This paper aims to assess the geochemistry of GCS, investigating the geological response of rock formations and brine to CO_2 injection. A critical evaluation of the different mechanisms for trapping, including structural aspects, capillary/residual trapping, solubility trapping, and mineral trapping, is conducted to assess their efficiency and applicability in sequestering CO_2 within geological formations. This study delves into mineralization processes, wherein the rock matrix reacts with CO_2 to form stable carbonate minerals, in addition to methods for enhancing trapping mechanisms. This paper also assesses challenges and opportunities in the geological sequestration of CO_2 and suggests future research areas to enhance the containment and storage of carbon dioxide.

A detailed understanding of the phase behavior of carbon dioxide in the context of GCS is crucial in understanding the geochemistry. This is because its phases influence its transportation within geological formations during the GCS process, as CO_2 can exist in multiple phases, including as a supercritical fluid, liquid, and gas, each with distinct properties and interactions with the rock matrix and brine solutions.

2. CO_2 Phases for Geological Storage

For geological storage, the gaseous state in which CO_2 exists in ambient conditions is not convenient for the following reasons: At ambient temperature, the condensation and precipitation of CO_2 from the atmosphere are impossible, unlike water vapor [33]. The volume can be reduced significantly by compressing it, which makes it easier to transport and store. As the depth increases, the volume of CO_2 will decrease in geological formations. As shown in Figure 1, the volume of CO_2 reduces from 100 units at the surface to 0.27 at a depth of 2000 m as it changes from a gas to a supercritical fluid. This is due to the rise in temperature and pressure as the subsurface depth increases, which leads to an increase in its density with depth [34].

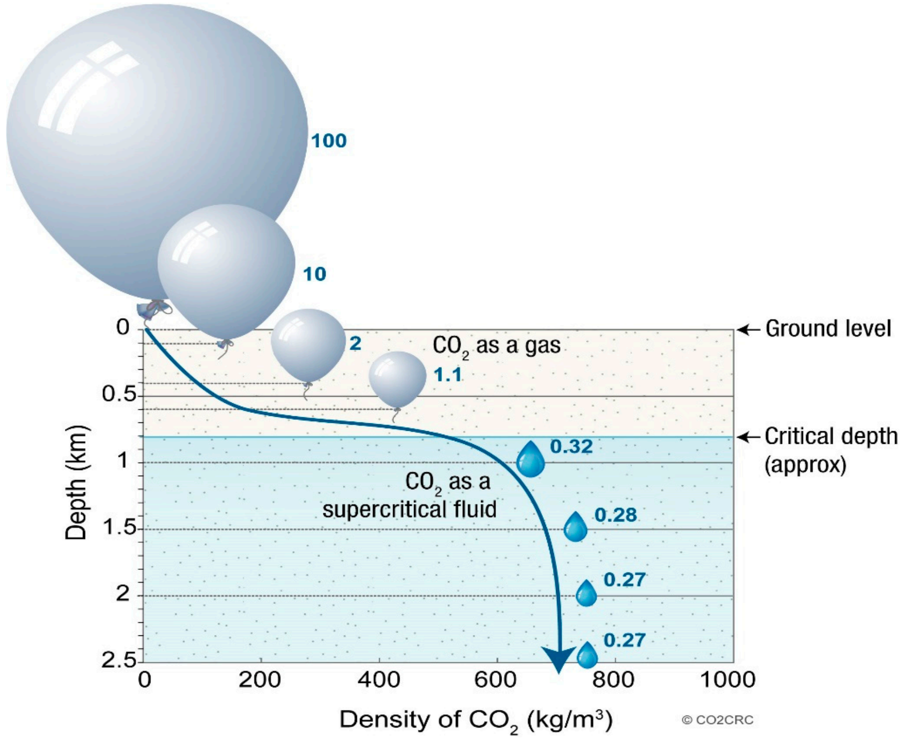

Figure 1. Reduction in volume of CO_2 with increasing depth [35].

In most sequestration situations (i.e., at a temperature of from −67 °F to 88 °F and at a pressure greater than 7.4 MPa), CO_2 is injected in a liquid form; however, when it is exposed to the formation's temperature and pressure, it becomes a supercritical fluid [36]. Supercritical CO_2 is a state that exhibits the properties of both a liquid and a gas. CO_2 reaches its critical point when subjected to a pressure of 7.4 MPa (1070 psi) and a temperature of 88 °F.

Supercritical carbon dioxide ($ScCO_2$) exhibits the following properties:

- Liquid-like density: It maintains a density like a liquid, which allows for dissolving it in a wider variety of formations than gaseous CO_2, and allows it to occupy less space.
- Gas-like viscosity: This phase exhibits a lower viscosity than its liquid phase (it is 15 times lower compared to pure water) [37] but a higher viscosity than its gas phase. This helps to improve its mass transfer properties and flow characteristics or enable its flow.
- Diffusivity: It exhibits higher diffusivity than liquid, which enhances the mixing and penetration of the formation. This means that CO_2 molecules in a supercritical state will spread out faster in the storage medium compared to those in a liquid state.

$ScCO_2$ optimizes its capacity for storage and reduces the issue of it escaping, since its density is higher than a gas but lower than a liquid [38,39].

The density of supercritical CO_2 (at a temperature of 88 °F and pressure of 7.4 Mpa) is 0.7 g/cm^3, which is significantly higher than its gas phase (two-thirds of the density of pure water), which enables it to occupy less pore space. This means that at a depth greater than 800 m, the density of CO_2 enables it to fill the pores efficiently and decrease the difference in buoyancy. Thus, geological storage sites should have a depth of this value to maintain the supercritical state of CO_2 [40–42].

The pressure and temperature of geological structures suitable for CO_2 sequestration are more significant than the critical point of carbon dioxide. Figure 2 presents a phase diagram of carbon dioxide, showing its critical temperature and pressure in aquifers, which are 304.2 K (87.98 °F) and 7.38 MPa, respectively. This indicates that CO_2, in this particular case, is at its supercritical state in storage [43,44].

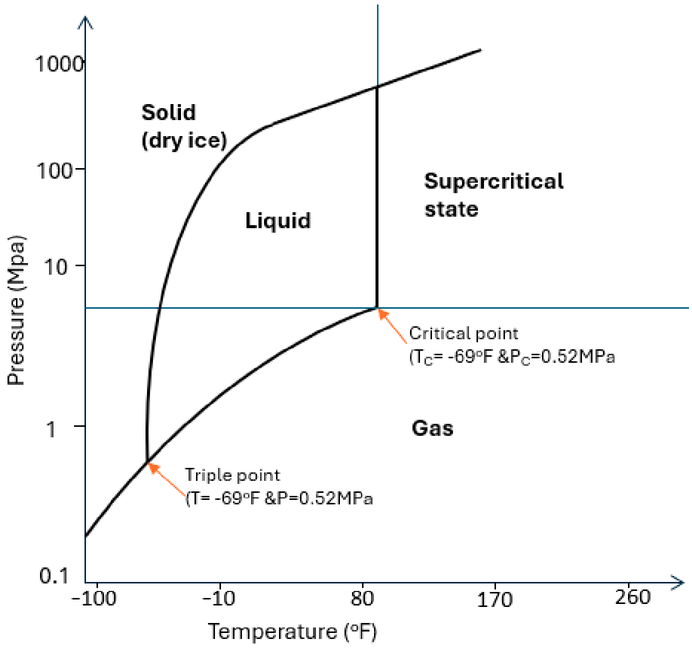

Figure 2. Pressure–temperature phase diagram for CO_2 [modified from [45]].

3. CO_2 Trapping Mechanisms for GCS

In GCS, CO_2 is injected deep underground, where it can be trapped in geological formations by various mechanisms to restrict its upward migration and leakage. The trapping mechanics can be classified as physical and chemical trapping mechanisms. In physical trapping mechanisms, carbon dioxide remains in its physical state following its injection. However, in chemical trapping mechanisms, the physical and chemical nature of CO_2 are changed as it reacts geochemically with the rock and formation fluid [46].

There are two physical trapping mechanisms: (1) static (stratigraphic or structural) trapping and (2) residual/capillary trapping. CO_2 forms a continuous fluid phase in static trapping, while in capillary trapping, it is in the form of an isolated CO_2 pocket or is non-connected. Similarly, there are two chemical trapping mechanisms: (1) solubility, or dissolution trapping, where CO_2 is dissolved brine, and (2) mineral trapping, where carbonate minerals are formed as a result of the chemical interaction between rock, CO_2, and brine [47–50]. In general, CO_2 trapping mechanisms can be classified into four main types: structural, residual, solubility, and mineral trappings, and these mechanisms are summarized in Table 2 alongside their descriptions, advantages, and challenges.

These four main trapping mechanisms have different storage capacities based on the storage period or time scale. Figure 3 presents the contributions of each trapping mechanism, starting from the time the injection stops. As shown in the figure, structural trapping initially has the largest share of CO_2 storage, and as time goes on, the contribution and storage security of the other mechanisms increases.

The trapping period can be represented as follows: $t_{structural\&stratigraphic} < t_{capillary} << t_{dissolution} < t_{mineralization}$.

Table 2. CO_2 trapping mechanisms during the geological storage of CO_2 [38,49,51–53].

Trapping Mechanisms	Description	Advantages	Challenges
Structural (stratigraphic) (in pore space)	• This is the first trapping encountered during geological sequestration, where CO_2 is trapped physically. • Supercritical CO_2 in its mobile phase is stored in geological structures with a caprock. • Trapping occurs due to the high capillary entrance pressure of CO_2.	• Gives a primary barrier against the upward movement of CO_2 so as to ensure its instant containment. • Stores significant amounts of CO_2 in a short duration.	• CO_2 can leak if there is a compromised caprock or failure in the seal. • There can be movement of CO_2 to other traps. • The integrity of the seal is affected during overpressure. • The integrity needs to be monitored regularly. • Only applied to selected rock properties.
Residual/capillary trapping (in flushed zone)	• As supercritical CO_2 passes through a pore in the storage formation, reservoir fluids are displaced. • CO_2 movement occurs upward because of density differences and laterally because of viscous forces. • Residual trapping occurs only when the CO_2 plume is mobile, as the CO_2 replaces brine [54].	• Improving storage efficiency while minimizing the mobility of CO_2. • Reduces possible CO_2 leakage root points and guarantees homogeneous CO_2 dispersal.	• For formations with low permeability, it is a slow trapping mechanism. • Continuous injection cycles of CO_2 could cause challenges over time. • Effectiveness of trapping can be affected by the presence of brine or oil.
Solubility trapping (in host brine)	• Results from the dissolution of CO_2 in the formation water or brine. • The dissolution results in the formation of CO_2-saturated brine. • The buoyancy force is eliminated once the CO_2 separate phase is over because of dissociation. • Compared to the reservoir fluid, the brine density increases as the CO_2 dissolves, which causes CO_2-saturated brine to sink to the bottom of the formation. • Weak carbonic acid is formed as a result of CO_2 dissolution.	• The dissolution of CO_2 improves storage security. • The mobility of CO_2 within the reservoir is reduced. • Precipitation reactions are generated, which trap CO_2.	• The capacity is limited since it depends on the solubility of CO_2. • There are significant changes in the density of water. • The water may be acidified, which can affects the rock and fluid properties. • Because of its complexity, it is difficult to predict the interaction of the minerals in the reservoir with the CO_2.

Table 2. *Cont.*

Trapping Mechanisms	Description	Advantages	Challenges
Mineral trapping	• Occurs as CO_2 changes to calcite. • Calcite is formed when CO_2 and solid minerals react. • Mineral trapping takes place after or during solubility trapping, which makes it a slow trapping mechanism. • Stores CO_2 permanently • Permeability and porosity of rock changes notably during this type of trapping [40,55].	• Enables permanent and secure CO_2 sequestration. • CO_2 immobility is guaranteed if it is converted into a solid mineral. • CO_2 does not occur in a separate phase, which avoids its upward movement by forming precipitates [56,57].	• Slow reaction. • The permeability affects the mineralization. • Affected by the existence of minerals and the reactivity in the storage reservoir. • The trapping process may affect the CO_2 solubility and reservoir integrity.

The CO_2 trapping potential differs significantly among diverse geological formations, and the suitability of formations for carbon storage varies accordingly. For instance, structural or hydrodynamic, dissolution, and mineral trappings are applied for sandstone and carbonate formations [58–60], whereas mineral and dissolution trapping are employed for basaltic formations [61–63]. On the other hand, diffusion and adsorption trapping are applied in coal seams, organic-rich shales, and clay interlayers [64].

In general, due to their storage capacity, saline aquifers are the most promising and widely applicable formations for GCS [46,65]. The following section explains mineralization in saline aquifers for GCS.

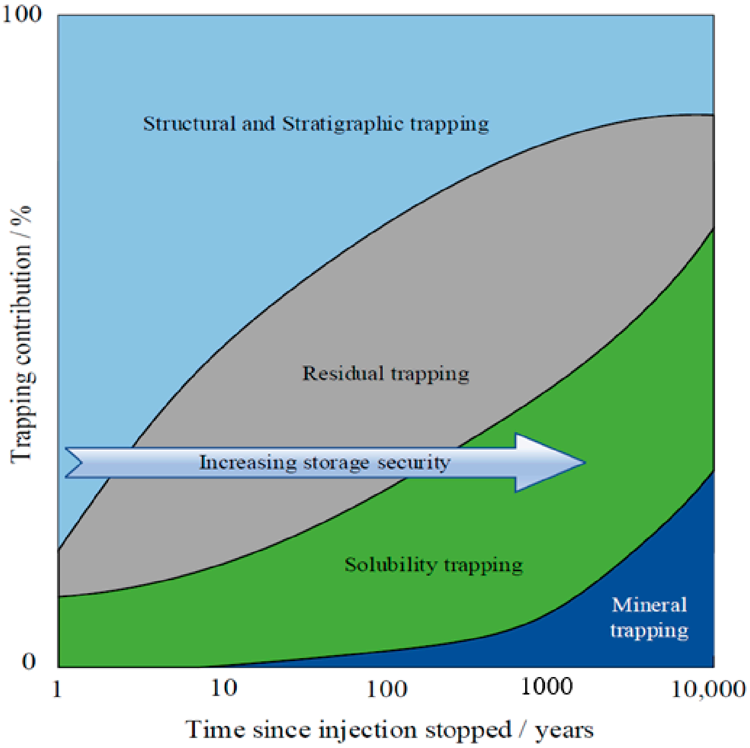

Figure 3. Security of CO_2 trapping mechanisms over time [66].

3.1. *Enhancing CO_2 Trapping in Saline Aquifers*

Saline formations are ideal for CO_2 sequestration because they have the following properties: high permeability, which enables CO_2 injection at high rates with no substantial increment in pressure; thick formations; and salinity, which fulfills groundwater protection regulations (greater than 10,000 ppm of TDS (total dissolved solids)) [13,67].

The three forces, buoyancy, viscous, and capillary forces, govern CO_2 trapping in aquifers (Kong et al., 2013 [51]).

Viscous forces are the primary forces during the injection phase of CO_2 and are responsible for the lateral and vertical movement of CO_2. The movement of CO_2 is caused by the pressure difference resulting from the injection of CO_2. In the post-injection phase, buoyancy and capillary forces trap the CO_2 [51].

3.1.1. Solubility Trapping

Solubility trapping refers to the dissolution of the injected CO_2 in the target formation, which means that solubility trapping is mainly affected by the dissolution of CO_2 in the formation fluid or brine [68].

For deep saline aquifers, the injected carbon dioxide moves upward to the interface between the caprock and reservoir, where it contacts the formation water, which causes mass transfer because of the dissolution of the CO_2 [69]. Dissolving CO_2 in brine is governed by diffusion at the interface between the formation water and the free gas phase. But, because the molecular diffusion coefficient is small, this process is very slow, and it could take thousands of years for the CO_2 to dissolve fully in the brine (formation water) [51]. The solubility of CO_2 is affected by the formation pressure, temperature, salinity, surface wettability, and injection rate [70]. An increase in pressure increases the solubility of the CO_2 in the brine, since it increases the density of CO_2. When the salinity decreases, the rate of CO_2 dissolution in the brine increases. This is because a low salinity results in fewer cations, and cations form hydrates, which act as a barrier for CO_2 dissolution. This is why solubility trapping is expected to be less effective in very salty formation fluids, typically associated with evaporite rocks. However, aquifers that have carbonate rocks promote the dissolution of CO_2 [8].

A reduction in temperature, a higher injection rate, and water-wet conditions enhance CO_2 dissolution [71,72]. The accurate modeling of CO_2 dissolution is crucial at the reservoir scale, rather than just at the pore level, in order to capture the complex dynamics of CO_2 storage. Additionally, it is essential to account for reservoir heterogeneity in these models, as it significantly impacts the solubility of CO_2 and makes the dissolution process highly dynamic [73].

There will be a considerable reduction in porosity due to the accretion of carbonates in the rock matrix and the induced alterations to the rock minerals resulting from the CO_2 dissolution. A slight decline in porosity could result in a considerable reduction in permeability, which, in turn, could reduce the injectivity of the CO_2 [57].

3.1.2. Enhancing Solubility Trapping

The main issue in solubility trapping during ordinary CO_2 injection is related to the buoyancy of CO_2. The density and viscosity of the injected CO_2 are lower than the formation water in standard CO_2 injection, which results in the upward migration of the CO_2. If the caprock integrity is compromised, this migration of CO_2 may result in long-term leakage risks, which are the main concern in the implementation of GCS projects [74]. Injecting a CO_2–brine mixture can mitigate the buoyant migration of CO_2. Solubility trapping can be enhanced by increasing the area of contact between the brine and CO_2 (through less viscous CO_2 fingering), flowing in heterogeneous reservoirs, or removing the denser CO_2-saturated brine below the CO_2 cap [75]. The contact area can be increased by mixing the CO_2 with brine before injection, which will prevent its migration, thus helping to maintain the storage site integrity [74,76].

On the other hand, solubility trapping can be used to unveil the potential of unconfined aquifers for GCS. A study by Addassi et al., 2022 [77], explained that solubility trapping can be applied to utilize abundant unconfined reservoirs for GCS. According to the study, the process involves injecting water-dissolved CO_2, which leads to instant solubility trapping. This mechanism mitigates CO_2 leakage in unconfined reservoirs, because once dissolved, the CO_2 will not migrate to the surface as it is not buoyant. The study by Addassi et al. used TOUGHREACT computer code to carry out the geochemical modeling by assuming an injection of 100,000 metric tons of water-dissolved CO_2 annually for 100 years into a porous rock at a depth of from 800 to 2000 m below the surface without a caprock, representing an unconfined sedimentary aquifer. In such cases, structural and residual trappings will be negligible, which means the early stages will be dominated by solubility trapping, and the later stages will be dominated by mineral trapping, as shown in Figure 4, where the green color indicates solubility trapping, and the blue color indicates mineral trapping [66] Injecting the dissolved CO_2 will resolve the CO_2 buoyancy challenge in GCS. In such a case, the storage reservoir is not necessarily deep, unlike with $ScCO_2$, and the caprock integrity is not an issue. This solubility trapping can alleviate public acceptance and storage security issues by mitigating leakage issues [76].

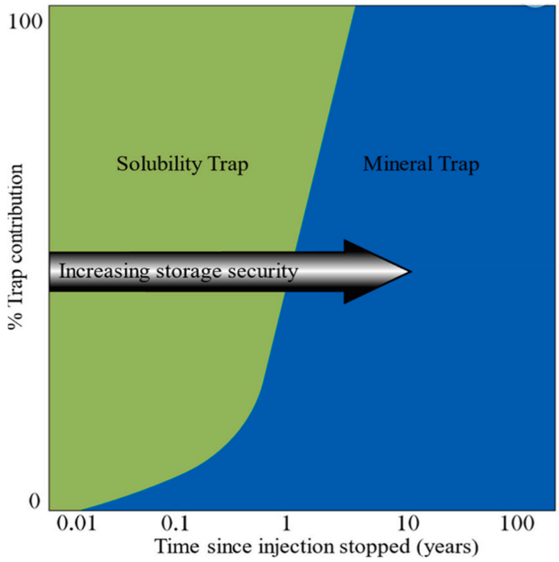

Figure 4. Solubility and mineral trapping in basalt formation [66].

3.1.3. Mineral Trapping

Like solubility trapping, mineral trapping is also one of the most promising long-term solutions for the geological storage of CO_2. However, although it is the safest and most reliable trapping mechanism, it is a slow process that can take thousands of years to occur. Deep saline aquifers have acidic formations with pH values of from 2 to 6, which is not convenient for the formation of carbonate minerals [78]. The pH level needs to be increased (higher than 9.0) for carbonate minerals to be formed, which can take thousands of years [21]. The main issue in enhancing the mineral storage capacity in mineral trapping is accelerating the precipitation during CO_2 sequestration [73]. There are several factors on which mineral trapping depends. These include the solubility of CO_2, the pore size, the mineralogy of the rock, the reactive surface area, the heterogeneity, impurities (H_2S, N_2, SO_2, No_x, O_2, Ar, N_2, and H_2) in the injected CO_2 stream, wettability, and interfacial tension (IFT). Mineral trapping is highly dependent on the brine water pH and ionic loading [21,79]. These factors can directly or indirectly affect the acceleration of mineral trapping. Hence, it is essential to investigate methods to accelerate CO_2 mineral trapping.

3.1.4. Methods to Accelerate CO_2 Mineral Trapping

- Increasing CO_2 solubility

Increasing the rate of mass transfer between the brine and CO_2 can increase its solubility. This can be achieved by mixing the CO_2 and brine before, during, or after its injection into the aquifer [50]. It is reported from the CarbFix project that carbon mineralization occurred within two years after dissolving the CO_2 in groundwater before or during the injection, which is an indication that injecting CO_2-dissolved brine can help to accelerate carbon mineralization [76,80].

- Co-injection of carbonate anhydrase (CA)

CA accelerates carbonate mineralization by decreasing the pH in the reservoir while catalyzing the reaction of CO_2 with H_2O to form HCO_3 and H^+. This results in a higher rate of CO_2 mineralization [81,82]. The most common biocatalysts for such applications are CA enzymes and CA (bio-generated) bacteria [83,84].

- Microbes

The reservoir where the CO_2 is to be stored can have microbes in it, and these microbes can affect the growth of carbonate minerals, specifically in oversaturated fluids [85]. Some of those microbial molecules enhance calcite growth, which can, in turn, be manipulated to mitigate CO_2 leakage [86,87].

Microbes can enhance mineral trapping by inducing the precipitation of carbonate minerals, decreasing the pH, or increasing the solubility. The potential growth of these microbes with long-term exposure to CO_2 can enhance CO_2 solubility and mineral trapping. However, further research should be conducted to study the effect of the interaction of these bacteria with CO_2–brine–rock systems [88]. These microbes include urea-producing bacteria, halophilic carbonate-forming bacteria, and indigenous microbes isolated from deep saline aquifers [88,89].

- Enhancing the surface area of reactive minerals

This is achieved through hydraulic fracturing during CO_2 injection, which increases the surface area in the injector wells. An experimental study by C.P. Zhang et al. revealed that CO_2-based fracking (CBF) can be used to enhance hydraulic fracturing. The experiment was conducted on a siltstone sample to investigate the difference in the fracturing efficiency of CBF with WBF (water-based fracturing) in unconventional gas reservoirs, and the results showed that CBF is a compelling choice for WBF in creating interconnected fractures [90]. This, in turn, increases the silicate dissolution rate, causing the mineralization of carbon in the storage formation [91].

- Selecting sedimentary reservoirs with reactive minerals

Hosting rocks rich in divalent cations exhibit accelerated mineral trapping. According to the study in [79], it is preferable to select geological formations with divalent metal ions or cations (Ca^{2+}, Fe^{2+}, and Mg^{2+}) for CO_2 storage in mineral trapping situations.

3.1.5. Residual/Capillary Trapping

In capillary trapping, when the CO_2 is injected into the saline formation, the gas saturation increases, and the gas pressure displaces the brine water. When the injection stops, the density difference between the gas and brine causes the gas to continue migrating upward and the brine to descend [46]. This leads to the brine (waiting phase) entering the pores, pushing the CO_2, and resulting in a significant volume of CO_2 being trapped in small clusters of pores. This leads to the permanent immobilization of the CO_2, which is called residual trapping [92].

As shown in Figure 5, the buoyancy difference between the brine and the gas makes the CO_2 gas move vertically to the top of the aquifer. The arrows show the path of the injected CO_2 to the left and right of the injection well. The buoyancy or density difference between the CO_2 and brine results in a high flow rate to the right side towards the top. The gas displaces the brine on this side since the gas saturation is increasing, and hence, there is the continuous motion of CO_2. However, on the left side, the CO_2 injected is totally trapped or immobilized, and this region becomes less permeable.

Studies conducted on the capacity of residual trapping have confirmed that such a mechanism could result in the trapping of high volumes of CO_2 by substantially inhibiting the movement of CO_2 [93,94]. Residual trapping has been demonstrated to be effective in cleaning sandstones and carbonates [95]. It is more effective compared to other short-term trapping mechanisms [96,97].

However, it is important to consider factors influencing the residual sequestration. Factors affecting residual trapping can be grouped into physicochemical, petrophysical, and operational factors. Physicochemical factors include the wettability and the interfacial tension between the CO_2 and brine, and these are affected by impurities in the injected gas, the pore structure of the saline aquifers, the pore pressure, and the temperature [73]. Petrophysical factors include the porosity and permeability, while operational factors include drainage and imbibition rates [98]. The immobilization of CO_2 is also affected by the ratio of viscous forces to gravity forces, heterogeneity, and the injection rate [99].

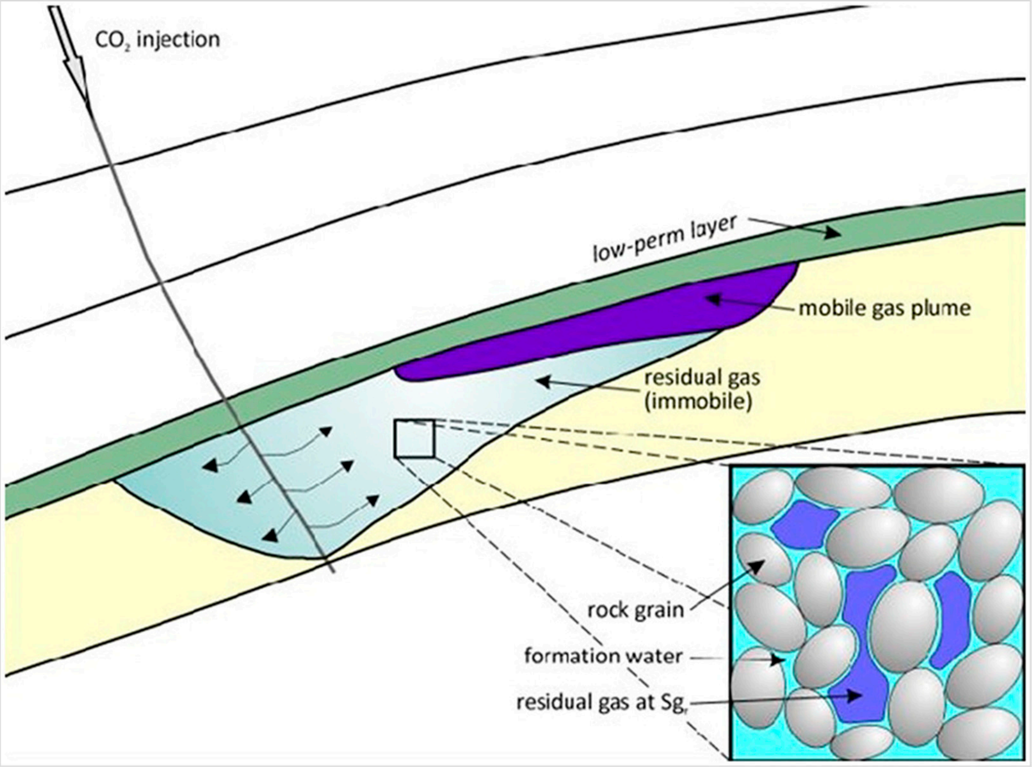

Figure 5. Schematic of the trail of residual CO_2 that is left behind due to snap-off as the plume migrates upward during the post-injection period [79].

The role of wettability in regulating the distribution of CO_2 saturation is very crucial. The study in [95] found that in oil-wet or intermediate-wet oil reservoirs, capillary trapping is less efficient compared to in deep saline aquifers, which exhibit water-wet characteristics in the presence of CO_2. The study demonstrated this by comparing residual CO_2 saturations in oil-wet sandstone with the equivalent water-wet sandstone, and it was found that the residual trapping efficiency in the oil-wet system was significantly lower. This is because the difference in the pore-scale capillary forces in such reservoirs reduces the capillary trapping capacity. On the other hand, a CO_2-wet state has a higher trapping coefficient compared with water-wet conditions [98]. The trapping coefficient, C, can be determined by using Equation (1) given below.

$$C = \frac{1}{S_{gr}} - \frac{1}{S_{gi}} \tag{1}$$

where S_{gi} and S_{gr} are the initial and residual CO_2 saturation, respectively.

Therefore, water-wet systems are preferable due to their better residual trapping capacity. Concerning rock types, many studies have suggested that sandstone formations have better residual trapping potential than carbonate formations [98].

In addition, solubility trapping and residual trapping are interdependent; hence, it is essential to consider the impact of solubility trapping while exploring residual trapping mechanisms [73,100].

3.1.6. Structural Trapping

In structural sequestration, large amounts of CO_2 are stored in a short period of time. This is commonly observed in reservoirs that have contained oil and gas for millions of years, where the volume of the pore space is the main factor affecting the storage capacity [101].

Structural trapping is the primary mechanism for inhibiting the migration of CO_2 from the injection point to other subsurface sites, which is undesirable for storage. Carbon dioxide is stored in a supercritical state and as a buoyant fluid beneath the caprock or next to a barrier that is impermeable. The difference in the densities of the brine and CO_2 makes the injected CO_2 flow upward under the action of buoyancy and then become blocked by the caprock. According to recent studies, if CO_2 is injected at a sufficient distance from the aquifer or reservoir boundaries, the necessity for structural trapping can be reduced [102].

The capacity of the structural trapping mechanism in saline aquifers should be assessed based on the CO_2 injection rate, the caprock properties, and on the basis of the actual geological conditions of the saline aquifer [73]. This is because in saline aquifers, the structural trapping capacity of CO_2 storage is dependent on the sealing capacity of the caprock, the capillary force of the caprock, the reservoir properties, the CO_2–brine interfacial tension, and the CO_2 injection rate [103].

During structural sequestration, the effect of the CO_2 injection rate can impact the pore pressure, which causes caprock damage and CO_2 leakage if not within the caprock's capacity. Thus, further research needs to be conducted to evaluate the reservoir's capacity based on the saline aquifer's actual geological conditions, caprock properties, and CO_2 injection rate [73].

In general, even though stratigraphic/structural trapping mechanisms are the main mechanisms for storing injected CO_2, they are less secure storage methods because there is a greater chance of CO_2 leakage. The risk of leakage will be minimized once the mineralization is started, since the CO_2 will not escape the reservoir [104].

4. CO_2 Mineralization in GCS

Mineralization, also known as mineral carbonation, involves injecting CO_2 into rock formations containing minerals that react with CO_2 to form solid carbonates, effectively locking away the CO_2 and preventing its release into the atmosphere. During mineralization, CO_2 is converted into solid carbonate minerals by chemically reacting it with divalent ions such as Ca^{2+}, Mg^{2+}, and Fe^{2+} [66].

Carbonates are very stable thermodynamically and can be stored permanently [105].

According to [105], the mineralization of carbon is the process of converting hydroxide and silicate minerals into carbonate minerals, where CO_2 can be stably sunk. This can involve ex situ (feedstock carbonation from its original location) or in situ (injection of CO_2 into the existing rock) mineralization processes [105].

Mineralization can be integrated with industrial processes to utilize captured CO_2 to produce valuable materials, such as construction aggregates or industrial minerals, thereby offsetting the costs of carbon capture and storage [106]. Mineral carbonation can be achieved by an in situ method, which is carried out by injecting the CO_2 into the geological formation, or by an ex situ method, where the carbonation is carried out above the ground in an industrial plant using previously mined or local rock [106,107]. In situ carbonation is a favorable option due to the availability of resources and its enhanced security. Also, this method does not require extensive mining. However, the main challenges are the geological characteristics and potential uncertainties regarding the caprock [106,108].

Novel and emerging techniques, including injecting dissolved CO_2 or CO_2 being injected as a nano-emulsion, can potentially enhance the mineral trapping mechanism by preventing $ScCO_2$ dry-out and reducing the necessity for deep reservoirs or secured seals [16].

In mineral trapping, gaseous CO_2 is converted into solid carbonate minerals, such as magnesite or calcite, through natural mineralization processes. Once the CO_2 comes into contact with the brine, it forms carbonic acid (H_2CO_3) or acidifies the formation fluid. H_2CO_3 is a weak acid that is ready to dissociate immediately, and the equation for the acidification of the brine is expressed as follows:

There are generally three steps in carbon mineralization, which are explained below.

1. Gaseous CO_2 is dissolved in an aqueous solution to form bicarbonate and carbonate ions. This step is further explained in the following equations.

The dissolution of the injected CO_2 in the formation water is shown in the following equations:

$$CO_2(g) \leftrightharpoons CO_2\ (aq) \tag{2}$$

$$CO_2\ (aq) + H_2O(l) \leftrightharpoons H_2CO_3(aq) \tag{3}$$

The dissociation of the CO_2 in the formation water makes the brine corrosive to any material in contact with it due to the formation of carbonic acid (the pH decreases to a value of about 3–5) [37,109].

$$H_2CO_3(aq) \leftrightharpoons H^+(aq) + HCO_3{}^-(aq) \tag{4}$$

$$HCO_3{}^-(aq) \leftrightharpoons CO_3{}^{2-}(aq) + H^+(aq) \tag{5}$$

As the pH is lowered, the dissolution of divalent-cation-bearing minerals is promoted. These minerals include pyroxene ($XYSi_2O_6$, where X and Y are either one or both divalent cations), olivine ($(Mg,Fe)_2SiO_4$), brucite ($Mg(OH)_2$), forsterite (dolomite + silica), kaolin ($Al_2O_3.2SiO_2.2H_2O$), and also plagioclase, illite, and smectite [89].

2. Cations such as Ca^{2+}, Mg^{2+}, and Fe^{2+} are released into the solution due to mineral dissolution.
3. Stable carbonates are formed due to ionic reactions at higher pH.

The pH increases back due to the dilution of $CO_3{}^{2-}(aq)$ in the formation water. Then, the carbonate ion and divalent cations form carbonate minerals (precipitation), which are represented by the following equations:

$$CO_2{}^{-3}\ (aq) + Ca^{2+} \leftrightharpoons CaCO_3(s) \tag{6}$$

$$CO_2{}^{-3}\ (aq) + Mg^{2+} \leftrightharpoons MgCO_3(s) \tag{7}$$

$$CO_2{}^{-3}\ (aq) + Fe^{2+} \leftrightharpoons FeCO_3(s) \tag{8}$$

It is also possible for the acidified brine to react with minerals such as silicate and carbonate in the rock to neutralize the brine. The equations are Equations (9) and (10).

$$H^+\ (aq) + CaAl_2Si_2O_8 + H_2O \rightarrow Ca^{2+}(aq) + Al_2Si_2O_5(OH)_4 \tag{9}$$

The dissociation of silicate mineral (anorthite) or silicate rock weathering to form kaolinite is expressed as follows:

$$H^+ + CaCO_3 \rightarrow Ca^{2+}{}_{(aq)} + HCO_3{}^-\ (aq) \tag{10}$$

Then, the reaction with carbonate minerals (calcium carbonate) occurs, forming bicarbonate, which happens in underground reservoirs.

The overall weathering can be obtained by combining the reactions in the above equations and can be expressed as follows:

$$CO_2 + CaAl_2Si_2O_8 + 2H_2O = Al_2Si_2O_5(OH)_4 + CaCO_3 \tag{11}$$

In this particular case, in Equation (11), one mole of the injected $ScCO_2$ is converted to calcite precipitate and sequestered in the geological storage, and the anorthite mineral is converted to calcite and kaolinite. For the precipitation to happen, there should be a sufficient dissociation of silicate minerals, as represented in Equation (9) above. The study in [110] reveals that calcite, being highly soluble in acidic environments, dissociates at a faster rate than dolomite and anorthite, while dolomite and anorthite dissociate more quickly than other minerals [110]. In addition, calcite is abundant compared to other minerals, and its dissociation alters the flow path and hydrodynamic properties [111].

Wet CO_2 is known for its corrosive potential, which affects the reservoir and its surroundings [112,113]. As the CO_2 injection pressure increases, the corrosion rate also increases [114].

When $ScCO_2$ dissolves in brine, its solubility increases nonlinearly with pressure and temperature, although it decreases with the salt content. The presence of impurities with injected CO_2, such as H_2S or SO_2, adds complexity to predicting the solubility of CO_2 in brine, requiring nonideal equations of state for accurate predictions [22].

Environmental factors like temperature, pressure, salinity, and impurity gases can significantly influence geochemical reactions at GCS sites. For instance, higher temperatures and pressures generally increase reaction rates, while impurity gases like H_2S can affect the brine pH and oxidation–reduction potential. Reservoir site-specific conditions, such as the composition of the reservoir rocks and the presence of reactive minerals, can also influence the extent and nature of the geochemical reactions during CO_2 injection in GCS operations.

The study by Jiemin Lu et al. [22] was conducted to study the effects of a reservoir site, and the following findings were obtained about this aspect. At the Weyburn CO_2-EOR site in Saskatchewan, Canada, the Frio pilot test site in Texas, and the Nagaoka pilot test in Japan, the aqueous concentrations of certain minerals like Ca, Mg, Fe, Mn, and HCO_3^- in the brine increased after CO_2 injection. This increase was attributed to the dissolution of silicate and carbonate minerals because of the reduction in the pH. The reduction in the pH was caused by the injection and dissolution of the CO_2 in the brine. On the other hand, at the Cranfield CO_2-EOR and sequestration site in Mississippi, lower rates of mineral reactions in the reservoir were observed, and the brine composition was almost unchanged during the CO_2 injection. This was because the reservoir rocks were composed of less reactive minerals like quartz, chlorite, kaolinite, and illite, with fewer reactive minerals like carbonates and feldspars present compared to other sites.

Moreover, microbial communities at geological storage sites can also impact geochemical reactions by mediating surface reactions, affecting redox reactions, and influencing the mobilization of organic compounds in aquifers [22].

A study by Raza et al. (2016) indicated that the presence of brine in the pore space during injection enhances the severity of geochemical reactions, thus reducing the magnitudes of the elastic parameters, including the shear modulus [115].

Likewise, the solubility of CO_2 in brine is affected by the temperature and pressure. A higher reservoir pressure increases the solubility, while higher temperatures lead to a lower solubility. This is because a higher pressure physically pushes more CO_2 molecules into the brine, which enhances the brine's ability to hold the CO_2 in solution. However, a higher temperature increases the movement of CO_2 molecules, making them more likely to escape the brine and become a gas.

On the other hand, a lower CO_2 injection rate can store more CO_2 [116].

Previous studies have shown that when CO_2 or CO_2-rich fluids are in contact with shale, mineral dissolution/precipitation will occur, which alters the pore structure [117,118]. Since shale formations are water-bearing formations, the presence of water may cause the CO_2 to cause more significant alterations to the shale pores. The alteration of the shale pores in the presence of both CO_2 and water is more important than their alteration in the presence of CO_2 alone.

In both cases (CO_2 and water and CO_2 alone), the shale porosity increases, and the increase in the porosity is greater when there is water and CO_2. This shows the effect of water in enhancing the reaction between CO_2 and rock [117,119].

Further research is still needed to assess the integrity of the pore alteration of shale after medium lengths of time or with seals under varying conditions involving different rock types and fluid compositions (including freshwater or brine) within the challenging environment of a storage site. Research should also address the robustness of the storage medium or seals when exposed to diverse rock types and fluid compositions (such as freshwater or brine) within the harsh environment of a storage site. Furthermore, further studies are necessary to understand how geochemical reactions may pose challenges during and after injection into a storage reservoir.

5. CO_2–Brine–Rock Interactions

CO_2, brine, and rock interactions are an essential component of GCS, and studying them can help to understand the long-term behavior of storage reservoirs. Since the injected CO_2 chemically reacts with the fluid and rock, the properties of the rock and the hydrocarbons will change. The type and salinity of the brine, the reactive surface area of the pores, and the contact time are some of the factors that alter the physical properties of the rock significantly during CO_2–brine–rock interactions. The study in [120] was conducted to identify which of these factors is dominant and the degree of influence of each factor. According to this study, the brine salinity is the dominating factor, followed by the time of exposure and the reactive pore surface area. In addition, many studies have found that geochemical interactions between CO_2, rock, and brine can affect the wettability of formations, help to immobilize the CO_2 via mineralization. and cause mineral dissociation and precipitation, which alter the petrophysical properties of the reservoir rock and the mechanical properties of the formations, including shale formations [121–124].

CO_2, brine, and rock interactions can significantly improve the wettability and alter the porosity and permeability. These two physical properties of rock directly correlate with the reaction time and carbonate content. On the other hand, the calcite content and soaking time increase the hardness of carbonate-rich rocks, while an increase in the soaking time decreases the tensile strength [125].

The effective porosity and permeability increase with the dissociation of the rock and decrease with the deposition of minerals and asphaltene minerals. This means that there will be a change in the oil recovery. According to the study by [126], in sandstone reservoirs, the percentage of asphaltene sedimentation, the mineral solution, and the oil recovery are higher in vertical configurations than in horizontal configurations. Also, minerals dissociate more with vertical injection than with horizontal injection.

Limestone can enhance the CO_2 storage potential because of the dissociation of the rock matrix compared to sandstone. However, because of its high permeability, sandstone reservoirs generate the strongest CO_2 foam compared to carbonate reservoirs, while CO_2 foam is an effective method for reducing CO_2 mobility in GCS applications by mitigating the flow stability [127]. On the other hand, limestone can generate more stable foam compared to sandstone [128].

In addition, if CO_2-rich brine is in contact with shale under in situ geological conditions, the formation mineralogy and pore structure of the shale change. As a coupled result, precipitation and mineral dissolution occur, increasing the pore volume, specific surface area, and pore size [129].

On the other hand, shale water wettability decreases when CO_2 is in contact with water and shale. This is because the carbonate and clay mineral contents of the shale decrease, while the quartz content increases significantly [130]. Thus, regulating the water wettability properly is required to meet CO_2 storage requirements. According to the study by [131], a prolonged $ScCO_2$ soaking time results in a reduction in the water wettability of shale. This reduction in the wettability may result in an increase in the breakthrough pressure of the CO_2, which may generate a CO_2 leakage during geological storage.

Before starting a geological carbon sequestration project, it is important to clearly understand how the CO_2–brine–shale interactions alter the pore structure [117]. A summary of the literature regarding the geochemical aspects of CO_2 storage is summarized in Table 3 below. The table summarizes the objectives and the key findings of each study.

Table 3. Summary of the literature on CO_2–water–rock interactions in GCS.

Author	Objectives	Key Findings
[132]	To review parameters influencing mineral trapping of CO_2 sequestration in brine.	• The effect of pH is higher during mineral trapping compared to the composition of the brine, system pressure, and temperature. • Carbonate mineral is more likely to form at $pH > 9$. • The effect of the system temperature is greater than the pressure.
[133]	To investigate the effect of CO_2 solubility on the rates of geochemical reactions.	• There is a reduction in the pH of the system due to CO_2 dissolution, but it is limited by the temperature rise and salinity. • As the temperature and pressure increase, the reaction rate also increases.
[134]	To investigate the effect of injecting CO_2 on the properties of the rock.	• The formation brine is acidified by the injection of CO_2 in storage formations, which induces chemical reactions with minerals. • The mechanical and hydraulic properties of the rock are altered due to the reaction.
[117]	To comprehensively analyze the pore structure of Yanchang shale by looking at the changes in the shale pore structure and mineral composition before and after the interaction.	• The specific surface area, pore volume, and fractal dimension of the shale decrease after the interaction of CO_2, brine, and rock because of siderite precipitate formation. • Self-sealing is induced by the interaction of CO_2, brine, and rock, which enhances the integrity of the caprock in GCS.
[119]	To explore the effects of sub-/supercritical CO_2–water mixture on shale's microstructural and mechanical properties.	• When shale is exposed to subcritical-/$ScCO_2$ and water, there is a reduction in the contents of carbonate and clay in the shale. • The effect of $ScCO_2$ is higher than $SubCO_2$ in terms of the alteration in the pore structure and the mechanical properties.
[135]	To ensure the maximum capture amount and long-term safety of CO_2 storage by numerically simulating artificial CO_2 injection for 30 years in a depleted oil reservoir (a case study).	• The dissolution process significantly reduces the amount of calcite present in the sandstone, which leads to improved CO_2 storage capacity. • The storage capacity of the sandstone and sealing capacity of the mudstone is enhanced by injecting CO_2. • To ensure safe and long-term GCS, depleted petroleum sandstone reservoirs with overlying mudstone caprocks are suitable.
[115]	To evaluate the changes in the variation in sandstone's geomechanical properties when exposed to $ScCO_2$ for a shorter duration.	• Injecting $ScCO_2$ into the pore space with brine enhances the severity of the geochemical reactions, reducing the magnitudes of elastic parameters, including the shear modus.
[24]	To measure the critical geochemical reaction parameters between injected CO_2–H_2S, reservoir rocks, and brine and their impact on the fluid and rock properties.	• There is a limited impact of the aging process on the sample porosity and permeability. • The results indicate observable changes in the rock samples for all H_2S concentrations.
[136]	To determine the kinetic rates of mineral dissolution, specifically for CO_2 injection in the presence of H_2S into carbonate formations.	• The introduction of H_2S up to a 500 ppm level had a minimal impact on the porosity and permeability of the core samples.
[137]	To examine the essential factors for using shale formations in CO_2 gas storage.	• Shale excels at CO_2 absorption. • Shale's pore structure is affected by the injection of CO_2.
[138]	To study the caprock's effect on the migration of CO_2 in carbonate clay. To assess the changes in the permeability of CO_2 after a breakthrough.	• Caprocks rich in clay affect the movement of CO_2, mainly via bigger pores. • The CO_2 permeability reduces after a breakthrough; however, there might be an increment later.
[139]	To examine the effects of organic acids on the rock wettability in CO_2 storage in sandstone. To assess the effect of nanofluids in enhancing CO_2 storage.	• Organic acids in geological CO_2 storage formations alter the rock wettability, but the change can be counteracted by using nanofluids. • The geo-storage efficiency and safety of CO_2 can be improved by pre-injecting nanofluids.

Table 3. *Cont.*

Author	Objectives	Key Findings
[79]	To assess how organic acids influence the CO_2 geo-storage efficiency in carbonate and sandstone. To study the capacities of nanoparticles to enhance the storage capacity.	• The storage security of CO_2 is altered by organic materials in storage sites. However, the utilization of nanoparticles can counteract these effects.
[140]	To investigate the interaction between caprock, CO_2, and brine in Qinshui Basin coalbed. Also, to validate the results from a geochemical simulation with experimental results for enhancing geological CO_2 geo-storage predictions.	• Considerable chemical reactions occur in coal seams as a result of CO_2 geo-storage. This results in the dissolution and precipitation of minerals. • Newly formed minerals like dolomite and siderite enable the permanent trapping of CO_2 and enhance the storage security by decreasing the porosity, which limits CO_2 leakage.
[141]	To assess how CO_2 injection impacts carbonate rock permeability.	• The well injectivity of carbonate formations is affected by the injected CO_2 since the precipitation reaction notably reduces the permeability in heterogeneous rocks.
[142]	To measure the effect of CO_2 injection on the reduction in the well injectivity in terms of the decrease in the core permeability.	• After injecting CO_2 into core samples, the change in the porosity is a function of the carbonate content, which means that samples with the highest carbonate content will have a higher rate of the increase in porosity compared with samples with a lower carbonate content.

6. Challenges in the Geological Storage of CO_2

For effective geological storage of CO_2, the selection of the storage reservoir site is crucial, and it is based on three main factors:

- Capacity: This is the pore volume available in the reservoir to store large amounts of CO_2.
- Injectivity: This is the ability of the storage formation to accept and pass CO_2. A formation with a high permeability and requiring lower wellhead pressures is the best option.
- Containment: This helps to ensure that the CO_2 injected is not leaked into the groundwater or does not escape to the surface since the CO_2 density is lower than the that of the formation brine. For this purpose, caprocks and sealing faults play an important role.

For geological sequestration, the ideal characteristics for the storage reservoir and caprock are being highly leak-proof, a large capacity for storage, efficient sealing, a fault-free stratum, and stability during and after injection [143]. It is standard to sequestrate CO_2 for at least 1000 years, with a leakage of less than 0.1% per year [117,118].

Although carbon capture and sequestration (CCS), or geological carbon storage (GCS) is the main viable option for reducing the enormous amounts of CO_2 in the atmosphere in order to mitigate the environmental effects of CO_2, there are risks, especially related to geological (geophysical and geochemical) processes if they are not properly understood and managed [76,144,145]. This is because the build-up of high pore pressures caused by the injected CO_2 can result in a change in the stress field, activating preexisting fractures, chemical alterations, and caprock–CO_2 pore fluid interactions. These risks could include caprock failures, well integrity losses, CO_2 leakage, ground and formation water contamination by dissolved CO_2, unwanted fault reactivation, induced seismicity, reservoir deformation, the precipitation of undesirable minerals, issues related to scaling-up geological storage projects, and public consensus on CCS projects. The major challenges associated with geological carbon storage are explained in the following sections.

6.1. Caprock Failure

Caprock is a critical barrier that traps the injected CO_2 within the storage reservoir, preventing its upward migration into the atmosphere or into shallower formations. The caprock should have an efficient sealing ability in order to prevent CO_2 migration. The sealing ability of the caprock is influenced by factors including the porosity, permeability, mineral composition, pore structure, and mechanical properties of the caprock. To maintain the containment of CO_2 over a long period, the caprock for a selected storage site should exhibit low permeability, low porosity, and a high capillary entry pressure. This ensures that the CO_2 will remain trapped by the capillary forces within the pores [146]. In addition, the rapid dissolution of carbonates during GCS should be considered, since they can corrode the caprock, cause leakage, and, hence, jeopardize the CO_2 containment [27].

Thus, enhancing the caprock sealing efficiency is a key focus in carbon capture and storage projects to ensure the long-term containment and safety of the injected CO_2 [147,148]. The tensile failure of the caprock and fault reactivation are the main mechanisms that can lead to CO_2 leakage, thus compromising the storage integrity [149].

6.1.1. Tensile Fractures

Caprock tensile failure is caused when the pore pressure is more than a specific threshold during CO_2 injection. The CO_2 injection rate is a function of the injectivity of the target reservoir. The injectivity index is defined by Equation (12).

$$I = \frac{q}{\overline{p}_r - p_{bh}} \tag{12}$$

where I is the injectivity index, q is the flow rate, $\overline{p}_r$ is the average reservoir pressure, and p_{bh} is the BHP, or the bottom-hole pressure.

The reservoir pressure has the largest impact on the injectivity. The injectivity can also be affected by factors like salt plugging, hydrate formation, and thermal fracturing. A tensile fracture may be induced if the downhole pressure exceeds the fracture pressure due to the injection rate. Well-stimulation methods like acidizing and hydraulic fracturing could solve this issue, since they increase the permeability near the wellbore [150]. If there is significant pore pressure buildup, the response may extend to the top of the target storage reservoir and potentially to the seabed or the surface. For impermeable caprock, the highest pore pressure buildup is expected at the caprock–reservoir interface, which leads to the possibility of shear failure at the interface.

6.1.2. Fault Reactivation

If the failure at the interface propagates to the caprock, the rock's stability can be significantly damaged. If a fault exists, there is the potential for reactivation during the injection of the CO_2. The caprock's stability can be affected by the fault within it (if there is one) or by the failure propagating from the fault.

Once the rock is not stable, there is the possibility of injecting CO_2 by buoyancy to the caprock–reservoir interface (the most exposed part of the shear failure) since the CO_2 is less dense than the formation water [148].

On the other hand, if the pore pressure buildup due to the injected CO_2 is severe, it will induce the reactivation of preexisting faults. Once reactivated, faults can act as a pathway for CO_2 and initiate micro-seismicity or even earthquakes [151].

6.2. Well Integrity Loss

In GCS, it is crucial to study whether the CO_2-induced geochemical reaction damages the well's integrity. Well integrity refers to the containment of fluid and pressure within the well or the capacity of the wellbore to be stable and leakage-free throughout its lifecycle. The most common CO_2 leakage channel is through the wellbore, which is why the wellbore is regarded as the main flow path in leakage risk assessment [152,153].

The primary factors that may cause leaks from various geological sites include the pressure, temperature, and geochemical reactions; however, a poor cement job is most likely the primary cause for CO_2 leaks during injection and storage from nearby the wellbore [154].

The concern about leakage is that CO_2-saturated fluid is incompatible with Portland cement and steel, which are used to prevent fluid migration to the surface. This is because the pH of Portland cement is greater than 12.5, while that of the CO_2-bearing fluid is less than 6 [155]. On the other hand, carbonic acid will cause corrosion to the low-carbon steel used for the casing [156,157].

One of the other main concerns of injecting CO_2 is that it could result in the corrosion and deterioration of the injection tubing, casing, and packing materials. Since there could be a leakage of the injected CO_2 via damaged cement or gaps between the casing and cement, a loss of well integrity is also a primary concern in CCS. CO_2 leakage may also contaminate fresh water [158]. Thus, monitoring the well integrity throughout the CCS process is important. According to the study by Su et al., the mechanisms of the well integrity loss or failure modes of CO_2 leakage from the wellbore can be categorized into three main groups, as shown in Figure 6 [159].

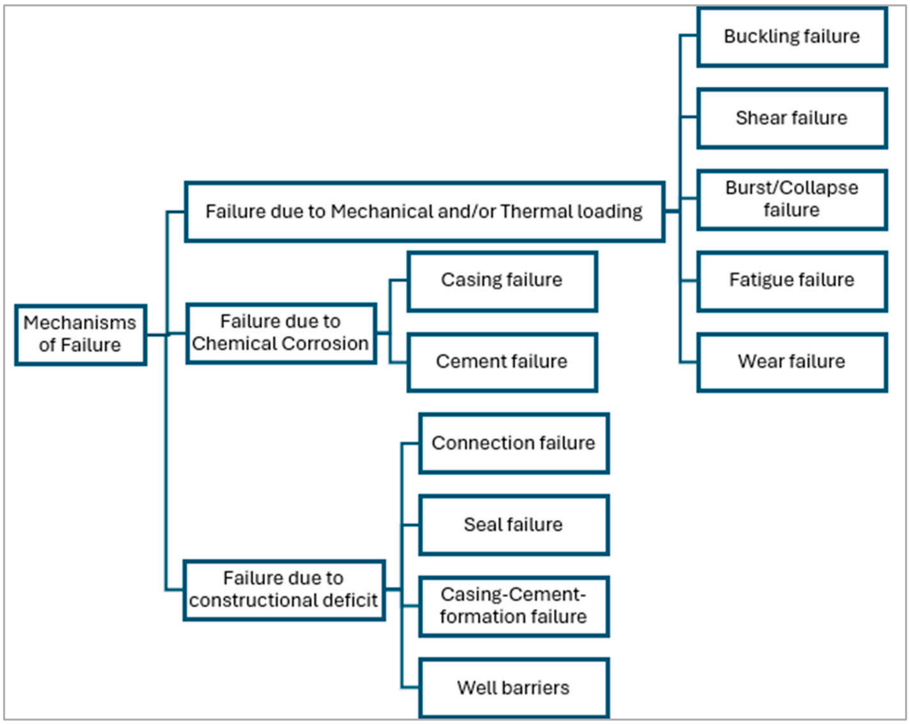

Figure 6. Main mechanisms for loss of wellbore integrity [modified from [159]].

Casing corrosion is due to the formation of carbonic acid as the injected CO_2 reacts with the brine in the reservoir. The chemical reaction is shown below.

$$CO_2(aq) + H_2O(l) \rightarrow H_2CO_3(aq) \quad (13)$$

As a result of corrosion, iron carbonate ($FeCO_3$) is formed, and the reaction is shown in Equations (14)–(17) below.

$$Fe \rightarrow Fe^{2+} + 2e \quad (14)$$

$$Fe^{2+} + CO_3{}^{2-} \rightarrow FeCO_3 \quad (15)$$

$$Fe + 2HCO_3{}^{-} \rightarrow Fe\,(HCO_3)_2 \quad (16)$$

$$Fe\,(HCO_3)_2 \rightarrow FeCO_3 + CO_2 + H_2O \quad (17)$$

Wellbore integrity is also an issue for repurposing aging or abandoned hydrocarbon fields for GCS.

6.3. Induced Seismicity

Many complex hydro-chemo-mechanical (HCM) interactions, such as mineral dissolution, water acidification, and alterations in effective stress, can occur in storage reservoirs during or after injection, potentially compromising the formation integrity over the short term or long term.

Experimental findings suggest that geochemical activity and CO_2 dissolution are notably greater in limestone, potentially increasing the porosity by approximately 16%. According to the research findings by Raza et al., 2019 [159], the reservoir strength decreases during injection in sandstone and carbonate rock types when exposed to CO_2. Significant differences in the geomechanical properties of sandstone were also observed after injection.

Deep underground saltwater reservoirs, often made of sandstone or carbonate rocks, are particularly suitable for storing CO_2 because the beneficial chemical reactions effectively trap the gas. However, these interactions create integrity problems in the GCS sites because they frequently result in changes to in situ stress and geomechanical changes. The infusion of CO_2 can dissolve it in the formation water and create carbonic acid, which considerably lowers the solution's pH [20,160]. As a result, quicker chemical processes cause the pore spaces to expand and reservoir rocks to lose strength [161].

Due to the build-up of pressure that occurs during and after CO_2 injection, geomechanical problems may also worsen. These problems could result in irreversible geomechanical changes, including fault reactivations, vertical uplift, and crack formation in the reservoir and caprock [160].

6.4. On Sorption and Swelling

Regarding the sorption and swelling of CO_2 in clays, several recent studies have demonstrated that the various clays and CO_2 interact, and clay minerals adsorb significant amounts of CO_2 [162].

While no visible seismic events had been reported from existing CO_2 storage projects until 2022, the potential for future commercial activities from large power plants raises the need for thorough geomechanical assessments. Geomechanical modeling plays a crucial role in guiding site selection, evaluating the risk of injection-induced seismic events and fault reactivation, and assessing uncertainties related to in situ stress fields and geomechanical properties. The risk of induced seismicity is expected to increase with the injection volume, highlighting the importance of best-practice guidelines for conducting site investigations, including historical seismicity documentation and risk mitigation strategies [163].

6.5. Leakage

The leakage of gas from subsurface storage sites is the main risk factor in underground sequestration of CO_2 or CCS projects in general. Although GCS is promising, this could be a barrier to its widespread application. Underground leakage must be maintained at 1% or less every thousand years, or continuous re-sequestration is required to have a GCS equivalent with low-emission projects [164]. Thus, understanding the effect of leakage on the geochemistry of the aquifer and the unsaturated (vadose) zone is essential in mitigating CO_2-induced geochemical challenges [164–166].

The intrusion of CO_2 into potable aquifers or unsaturated zones may lead to favorable or unfavorable outcomes. From a desirable outcome perspective, significant evidence has indicated that CO_2 intrusion can lead to the immobilization of some contaminants by altering their chemical form and improving their integration into stable mineral phases or by improving the precipitation of appropriate sorbents. On the contrary, there is strong evidence suggesting that CO_2 intrusion could be deleterious due to the mobilization of certain contaminants when contaminant-bearing minerals dissociate [92,165]. Indeed, there is still a significant knowledge gap in studying the effect of geochemical factors, including the inflex rate of CO_2, reduction–oxidation (redox) situations, the compositions of the gas stream, mineralogy in CO_2-induced reactions, and microbial activities [165].

In general, CO_2 leakage issues can be divided into geological and engineering leakage problems. As shown in Table 4, geological CO_2 leakage issues involve natural pathways like fractures and faults in geological formations, while engineering CO_2 leakage issues arise from failures in containment structures such as wellbores and injection processes.

Table 4. Main categories of CO_2 leakage problems.

Geological CO_2 Leakage Issues	**Engineering CO_2 Leakage Issues**
Leakages, natural fractures, and faults	Leakage due to wellbore integrity failure
Leakages across caprocks	Leakage through injection-induced fractures
Leakage through unconfined lateral migration	Leakage due to storage site overfill
Leakage due to volcanic and tectonic activities	Leakage due to post-storage disturbance

6.6. Detecting Leakage

The primary factors that could lead to leakage during injection and storage are geochemical reactions, pressure, and temperature. In regions near the wellbore, poor cement jobs could also be a reason for CO_2 leakage [154]. The existence of abandoned wells, aquifer over-pressurization, fractures, and faults could result in CO_2 leakage [51,76].

On top of the solubility and buoyancy of CO_2, which have been discussed in previous sections, CO_2 leakage during storage operations can be prevented by considering the following factors [13,167,168]:

- Geological Characteristics: These include the permeability and integrity of the caprock, which has a critical role in containing the injected CO_2 within the reservoir.
- In-situ Stress Variations: Variations in the magnitudes of stresses across different formations can impact the geomechanical response to CO_2 injection and influence the potential for induced fractures and CO_2 leakage.
- Mechanical Heterogeneity: Incorporating a three-dimensional distribution of the mechanical properties in the geochemical modeling can lead to a stochastic distribution of fractured zones and affect the CO_2 distribution near the injection well, thus influencing the potential for CO_2 leakage [168].

Leakage detection can be effectively achieved by monitoring how the pH changes as the low-pH region enlarges with the continuous injection of CO_2. Observing these pH variations makes it possible to track the migration of CO_2, providing an early warning for potential CO_2 leakage [169]. Once the leakage is detected during monitoring, controlling the migration of CO_2 is the next step.

According to the study by [170], there are two groups of technologies proposed to restrain the unwanted migration of CO_2 through different leakage channels. These are high-viscosity fluid-based and low-viscosity fluid-based barrier formation. High-viscosity fluid-based barriers include cement, gels, geopolymers, and nanoparticles. These are applied to block engineering-based leakage pathways. Since they are stable under CO_2 storage conditions and able to tolerate acidic (low-pH), high-dissolved-salt, and high-temperature conditions, geopolymers are proposed to replace cement. Low-viscosity fluid-based barriers, on the other hand, are proposed to be suitable for remediating leakage through natural pathways. These include biomineralization, hydraulic barriers, and chemically reactive barriers [170].

Another study by Manseau et al. [171] categorized the mitigation and remediation technologies for mediating undesirable CO_2 migration from geological storage units as follows:

- Interventions: re-establishing the integrity of active or abandoned wells through intervention. This includes replacing the packer, repairing the wellhead, tubing, squeeze cementing, well killing, casing patching, swaging, and well plugging and abandonment, managing abandoned wells, and preventing CO_2 blowouts.
- Fluid management mechanisms: This is carried out to counter the cause of leakage and/or to remove the leaking fluids. This could include hydraulic barriers, pressure

relief in the storage formation, residual trapping and CO_2 plume dissolution, and CO_2 back-production.
- Emerging/breakthrough technologies: These provide mitigation opportunities to control the undesired migration of CO_2. These include conventional Portland and geopolymer cement, foams and gels, nanoparticles, and biofilms.
- Remediation techniques are used to mediate the impacts potentially induced by such a migration.

6.7. CO_2 Impurities

A major concern in evaluating the safety of CCS projects involves assessing the influence of impurities present in the CO_2 stream [43]. A CO_2 stream will have impurities or co-contaminants depending on the efficiency of separation and purification technologies. These impurities could be H_2S, SO_2, NO_x, or mercury [172].

Also, CO_2 streams from natural gas processing or other industrial sources frequently contain H_2S [173,174]. CO_2 purity for subsurface storage relates to the well integrity, injectivity, and long-term storage integrity [24].

In a depleted reservoir where the hydrocarbon column has been replaced by water, injecting CO_2 into the water-bearing reservoir can induce acidic conditions and potentially lead to reactions with the formation, resulting in formation damage, especially if the reservoir is of a carbonate formation. Impurities like H_2S and SO_2 are known to have a higher chemical reactivity. Hence, when these impurities dissolve in the water, they form stronger acids and can cause more severe damage to the storage site.

Impurities can lower the density of the supercritical CO_2 stream, leading to reduced CO_2 dissolution in the water and consequently reducing the overall storage capacity of the reservoir [172]. Impurities can also change the reservoir permeability, porosity, and mineralogy, which could affect the integrity and efficiency of storage [175,176].

Understanding CO_2–water–rock reactions during CO_2 storage has been the subject of numerous studies, but less is known about mixed CO_2 and H_2S sequestration under typical oil and gas reservoir conditions [24].

Allowing contaminants in the gas stream is a desirable option since it lowers the capturing cost, which is the most expensive phase in CCS. Precipitation reduces the rock porosity and permeability, affecting the injectivity and, ultimately, storage capacity [176,177].

7. Opportunities and Prospects of Geological CO_2 Storage

7.1. Wellbore Leakage Risk Management in Geological CO_2 Storage

Risks due to the leakage of CO_2 in the wellbore can be managed by first identifying the leakage and then evaluating, monitoring, and handling it [159].

- Leakage risk identification: This step involves identifying the possible failure mechanisms of the wellbore that could lead to CO_2 leakage risks. Methodologies such as the Features (physical components), Events (incidents), and Processes (FEP) method, fault tree analysis (which involves constructing a fault tree that represents various failure modes), and quantitative risk evaluation models are commonly used to outline risks associated with wellbore integrity.
- Leakage risk evaluation: The next step is to evaluate the magnitude of the CO_2 leakage risks after identifying the potential risks. This can be achieved through quantitative risk evaluation models that assess the likelihood and impact of wellbore failures leading to CO_2 leakage.
- Leakage risk monitoring: This involves various techniques to detect and assess the presence of CO_2 leakages in CGUS. Some common types of leakage monitoring methods include the following:
    - ○ Atmospheric monitoring: This involves measuring the CO_2 concentration in the atmosphere surrounding the storage site to detect any leaks that may occur. Techniques such as radiocarbon (in CO_2) measurement and integrated sampling are used to identify increased levels of fossil-derived CO_2, indicating

    potential leakage. The atmospheric monitoring method has the capacity to detect 1000 tons of CO_2 leaks per year that can be 200–300 m away from the site in the daytime and greater than 600 m away during the night [178].
    - Surface deformation monitoring: This is carried out to detect potential leakages by measuring the changes in the surface topography. It involves measuring the soil gas flux, conducting soil gas surveys, and using remote sensing technologies to detect CO_2 emissions at the ground surface. These methods help in investigating gas movement, mapping fault zones, and monitoring the escaping CO_2 along particular pathways.
    - Time-lapse monitoring: Time-lapse monitoring involves comparing data collected at different time intervals to track changes in the CO_2 distribution and migration within the storage reservoir. Techniques such as InSAR (Interferometric Synthetic Aperture Radar) and 4D seismic surveys are used to monitor the evolution of the CO_2 dynamics and assess the integrity of storage sites.
    - Subsurface monitoring: This involves tracking the behavior of CO_2 within the storage site and assessing its integrity. It includes pressure sensors, cross-hole seismic monitoring, 4D seismic surveys, and advanced measurement techniques like CBL (Cement Bond Logs) and USIT (Ultra-Sonic Imaging Test) to assess the wellbore integrity and detect potential CO_2 leakage within the subsurface reservoir. To prevent the possible leakage of CO_2 into the USDW (underground source of drinking water), the chemical composition of the groundwater should be continuously monitored during the pre-injection, injection, and post-injection phases, and measurements should be taken. These measurements include measuring the pH, salinity, temperature, electrical conductivity, dissolved oxygen, and oxidation–reduction potential.
- Leakage handling: When CO_2 leakage is detected or when there is a potential risk, it is mandatory to take appropriate actions to address the situation effectively. This may involve implementing corrective actions to mitigate leakage, such as repairing the wellbore cement or applying a sealing agent, cement slurry injection, packer maintenance, wellbore integrity assessments, and establishing operational protocols.

Injecting CO_2 in a supercritical state is one method of mitigating well integrity issues. According to a study by U. Bilardo (2007), supercritical CO_2 protects wells because it is dry and non-corrosive [179].

However, it is important to note that supercritical CO_2 can be more expensive and cause problems with temperature fluctuations, which can cause the rocks near the wellbore to fracture both thermally and hydraulically [180].

7.2. Using Sealant Materials as a Leakage Remediation Technology

The leakage of CO_2 is a prominent challenge in geological CO_2 storage. Leakages may occur during or after the sequestration process through caprocks, wellbores, and reservoir fractures/faults of geological CO_2 storage, leading to environmental issues. Different types of sealants have been introduced and used to mitigate these issues. Sealants of different kinds have been developed and applied to minimize these hazards. Seven categories of sealants are currently used to alleviate the unwanted upward movement or leakage of CO_2 plume. These include gels, foams, Portland cement, geopolymer cement, biofilms, resins, and nanoparticles, which are applied to prevent leakages from different areas. Portland and geopolymer cement are used to treat the wellbore and regions near the wellbore by direct plugging, whereas resins are used for loss circulation, and cement additives are used for treating the wellbore and near-wellbore areas. Other sealant materials include the following: gels, which are used to treat leakages through tiny fractures and permeable media and are also used for casing repairs; biofilm barriers, which seal wellbore leakages in the formation; nanoparticles, which are used to treat the wellbore and reservoirs; and foams, which are used to treat leakages through porous media [42].

CO_2 is also used to treat sealings through porous media since it has a self-sealing nature at low temperatures.

According to the finding by Zhu et al., 2021 [41], future efforts and research are required to improve the long-term stability of polymer gels under high-temperature- and high-pressure-CO_2 conditions. These studies are needed to carry out the development of foams strengthened by gels for CO_2 leakage control in porous media, to investigate the selection and development of suitable bacteria for biotechnology applications in CO_2 leakage control, to emphasize environmental friendliness and stability in high-pressure supercritical CO_2 environments, and to advance and utilize the potential of nanotechnology to enhance the sealant performance [42].

7.3. Improving Seal Integrity to Prevent CO_2 Leakage

Another crucial strategy to prevent CO_2 leakage challenges in GCS is improving the seal integrity. Wellbore sealant selection is key to the long-term sequestration of CO_2, especially in injection wells. It is important to have a proper design of the cement system, not only in the short term but also for future conditions, in order to maintain the seal integrity or well integrity. Innovative cementing methods, including protective layers and optimizing the cement location and length, can significantly enhance the sealing capacity during CO_2 injection. Also, since legacy wells, especially with shallow surface casings, can act as passages for CO_2 to escape through, it is important to consider these during site selection [181]. According to the study by [182], in the case of abandoned wells, removing the casing steel from the wells is recommended before the final cement plugging and injecting a CO_2-resistant polymer to improve the seal integrity. The sealing integrity can also be enhanced by using chemical methods or by using CO_2-sensitive chemicals, which can be coupled with other methods, like cementing, to enhance the sealing of leakage pathways. According to the study by [183], CO_2 will initiate a reaction in CO_2-sensitive chemicals when CO_2-sensitive chemicals encounter a CO_2 leakage, which leads to the forming of a gel or solid structure inside the leakage paths.

On the other hand, although geochemical reactions with CO_2 is a challenge, shale caprocks demonstrate effective sealing capability during CO_2 storage. This means that shales can effectively prevent CO_2 leakage by maintaining their structural integrity over time [184].

7.4. Enhanced Oil Recovery (EOR)

Storing CO_2 through enhanced oil recovery (EOR) is another important method, since the petroleum industry has demonstrated its economic value for about 50 years [42].

CO_2 injected into oil reservoirs is miscible with oil and acts like a solvent. It reduces the oil's viscosity by causing the oil to swell and makes it easier to flow or extract. This benefits the environment by storing CO_2 and creates economic incentives for oil companies. EOR enables additional recovery, ranging from 7% to 23% [185]. A total of 50 to 67% of the injected CO_2 is returned to the surface together with the produced oil and gas and is then be separated and reinjected into the reservoir. The remaining portion of the injected CO_2 is retained in the reservoir by different mechanisms [186].

CO_2 becomes a valuable product when used for EOR, potentially generating revenue from its sale. Employing CO_2 for EOR can also enable oil and gas companies to prolong the production life of their fields, maximizing resource extraction while contributing to CO_2 storage, which is called carbon capture utilization and storage (CCUS) [38]. This approach provides a win–win situation for the environment and the oil industry. During CO_2-EOR, the CO_2 extracted from the well is separated and reinjected back to the reservoir, which then recurs in a cyclic manner.

7.5. Geochemical Monitoring for GCS

The geological sequestration of CO_2 highly depends on robust monitoring techniques to ensure its safe and permanent storage for an extended period. A variety of technologies have been developed for the effective monitoring of CO_2 leakages. A study by Chen 2018 mentioned four monitoring techniques, which include pressure monitoring, measuring of the near-surface soil CO_2 flux, shallow groundwater chemistry monitoring, and micro-seismic and cross-well seismic surveys [187].

According to the study mentioned above, effective monitoring involves determining the optimum location to place the monitoring well and determining the types of data to be measured. These data could include the electrical conductivity, CO_2 saturation, pressure, and temperature. The study also indicated the role of machine learning in reducing the computational cost of data assimilation in the monitoring design for geological CO_2 sequestration as follows:

- Optimize monitoring approaches by efficiently processing large amounts of data and identifying patterns that can inform decision-making processes.
- Streamlining data processing tasks, such as filtering and assimilating monitoring data, leading to faster and more accurate decision-making in monitoring design.

Another study by Massarweh and Abushaikha in 2024 identified basic approaches for the monitoring and assessment of CO_2 trapping at different stages of CCS projects. These include seismic and borehole geophysical methods, atmospheric monitoring methods, and laboratory-scale experiments [46].

These methods can be categorized based on the different stages as follows:

- Baseline (pre-injection) monitoring, which includes the following:
    - Borehole Geophysical Monitoring Techniques: These techniques are used for assessing geological CO_2 trapping in subterranean reservoirs.
    - Seismic Studies: These are conducted before CO_2 injection to collect site-specific data for predicting geological and geochemical trends.
- Injection monitoring, which includes:
    - Seismic Monitoring: This is carried out during actual CO_2 injection to monitor the changes in the reservoir. Seismic monitoring includes four-dimensional (4D) monitoring, four-dimensional–three-component (4D-3C) seismic technology, cross-well seismic tomography, time-lapse well logging, and passive seismic monitoring.
    - Borehole Geophysical Monitoring: This is carried out during injection to assess trapping mechanisms.
- Post-injection monitoring, which includes:
    - Atmospheric Monitoring Methods: These are valuable for monitoring CO_2 released from subsurface sources to the atmosphere after injection.
    - Lab-scale Experiments: These are used to examine the post-injection characteristics of CO_2 trapping.

Integrating experimental analysis with modeling and simulation is essential for obtaining a detailed understanding of the geochemistry in GCS. Experimental analysis allows researchers to investigate various aspects of CO_2 behavior within geological formations in a controlled laboratory setting. Experimental modeling includes core flooding experiments to determine rock permeability, studying CO_2–brine interactions, and studying mineral trapping and geomechanical testing to evaluate the mechanical response of rock formations to the increased pressure associated with CO_2 injection, including rock-induced seismicity and fracture development. There are limitations in experimental analysis, which include the complex nature of rock–brine–CO_2 interactions and the difficulty of replicating real-world conditions in the lab. Modeling and simulation in geochemistry can fill the gap in lab experiments and help to understand the long-term geochemical behavior of CO_2 storage sites [188].

Simplifying the geochemistry model should be carried out based on lab mineralogy data; if not, oversimplification of the model will lead to the misinterpretation of some active geochemistry processes in the model, resulting in erroneous results in the simulation.

In addition, a minimum of three to five minerals should be considered in geochemical models, as a very small amount or zero dissociation of minerals will occur if there is only one mineral in the model [49].

8. Conclusions

Storing CO_2 in geological formations, including depleted oil and gas reservoirs, saline aquifers, unmineable coal seams, basalt formations, and hydrate storage, offers a significant opportunity to combat climate change.

Geochemistry plays a substantial role in implementing effective geological CO_2 storage. It encompasses chemical interactions (between CO_2, the formation fluid, and the reservoir rock), mineral dissociation and precipitation, trapping mechanisms, and the effect of alterations to the mineral surface properties on fluid flow, each of which needs to be studied for the safe and effective implementation of GCS.

Various trapping mechanisms function cyclically to ensure the enduring containment of CO_2. Immediate containment relies on physical trapping mechanisms like static and local residual trapping. Conversely, chemical trapping, encompassing solubility trapping and mineral trapping, entails the interaction of the CO_2 with the formation fluid and minerals to ensure permanent sequestration. CO_2 can be permanently trapped in the subsurface region over time, and the trapping mechanisms reduce the mobility of the CO_2 and its potential to impact underground sources of drinking water (USDW) or to return to the atmosphere. Solubility, where CO_2 dissolves in the storage fluid, and mineral trapping, where CO_2 interacts with rock minerals to form a stable carbonate rock, are the most promising long-term solutions in GCS. Investigating the effects of parameters like wettability, heterogeneity, formation pressure, salinity, temperature, rock mineralogy, injection rate, impurities in the CO_2, the acceleration of mineral trapping, and increasing the dissolution rate of the CO_2 could enhance the effectiveness of GCS.

To ensure successful sequestration, the long-term stability of stored the CO_2 while minimizing environmental risks is crucial, as is developing effective monitoring and verification techniques designed to track geochemical changes during the GCS process.

In general, performing geomechanical analysis during the GCS process is paramount to assessing the interaction of the injected CO_2 with the rock and existing fluid, minimizing risks, ensuring effective monitoring, and ensuring safe and optimized storage.

9. Recommendations for Future Work

- The limited availability of published studies on the geochemical effects of CO_2 under in situ reservoir conditions, including the optimization of CO_2 trapping, necessitates further research to gain a more comprehensive understanding of the geochemical processes that occur during CO_2 storage in reservoir rocks.
- Since storage requires pure CO_2 streams, future advancements need to be made to make GCS techniques more affordable to compete with other carbon-free energy options.
- Even though many studies have been conducted to comprehend the interactions between the rock water and CO_2 during CO_2 storage, there is a knowledge gap regarding mixed CO_2 and H_2S sequestration under typical oil and gas reservoir conditions. Thus, studies need to be conducted to explore the effects of CO_2 impurities on GCS. It is also essential to carry out a sensitivity analysis to evaluate the effects of longer CO_2-H_2S aging periods on rock samples and reliability across a broader range of H_2S concentrations. In addition, the collective effects of the rock properties, such as the porosity and permeability, on the trapping efficiency should be studied, and a clear correlation should be established.
- A thorough geomechanical analysis still needs to be conducted with excessive courtesy as it would help to assure the absence of leakage when CO_2 approaches the seal because of buoyancy. This would help in examining whether the leakage (which could be due to the pressure of the CO_2) is high enough to overcome the entry pressure of

the seal and cause caprock fractures. Geomechanical analysis also helps in studying the caprock thermal stresses.

- Solubility and mineral trapping are the most promising long-term solutions for geological CO_2 storage. Hence, accelerating mineral trapping and increasing the solubility of the CO_2 in the reservoir fluid are significant for enhancing effective GCS through such trapping mechanisms. Thus, further studies should be conducted on accelerating mineral trapping and increasing solubility.
- Microbes could potentially impact effective GCS by enhancing solubility and mineral trapping. Therefore, conducting in-depth research to understand and apply microbes to enhance mineral trapping is essential.
- As leakages are the main challenge in the geological storage of CO_2, it is essential to further study all the mechanisms and potential pathways for leakage, including faults, fractures, failure of injection or other wells in the storage sites, and abandoned wells, as well as to assess the potential for caprock breaches, CO_2 migration, and groundwater contamination and its mechanisms.

Author Contributions: J.W.F.: writing, conceptualization, original draft, review and editing; H.E.: supervision, review and editing; A.H.: review and editing; D.M.F.: review and editing; S.R.T.: review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

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

References

1. ASHRAE Task Force for Building Decarbonization Carbon Sequestration. 2021. Available online: https://www.netl.doe.gov/sites/default/files/netl-file/co2_eor_primer.pdf (accessed on 24 February 2024).
2. Hurlbert, M.; Osazuwa-Peters, M. Carbon capture and storage in Saskatchewan: An analysis of communicative practices in a contested technology. *Renew. Sustain. Energy Rev.* **2023**, *173*, 113104. [CrossRef]
3. Osman, A.I.; Hefny, M.; Abdel Maksoud, M.I.A.; Elgarahy, A.M.; Rooney, D.W. Recent advances in carbon capture storage and utilisation technologies: A review. *Environ. Chem. Lett.* **2021**, *19*, 797–849. [CrossRef]
4. Adoption of the Paris Agreement. Available online: https://unfccc.int/resource/docs/2015/cop21/eng/l09r01.pdf (accessed on 14 July 2024).
5. International Energy Agency. 20 Years of Carbon Capture and Storage-Accelerating Future Deployment. Available online: https://www.iea.org/reports/20-years-of-carbon-capture-and-storage (accessed on 10 April 2024).
6. Vargas Guzmán, E.L.; Sant'Anna, L.G. Integrated assessment of global carbon capture, utilization, and storage projects. *Int. J. Greenh. Gas Control* **2024**, *131*, 104031. [CrossRef]
7. Kammerer, S.; Borho, I.; Jung, J.; Schmidt, M.S. Review: CO_2 capturing methods of the last two decades. *Int. J. Environ. Sci. Technol.* **2023**, *20*, 8087–8104. [CrossRef]
8. Delerce, S.; Marieni, C.; Oelkers, E.H. Carbonate geochemistry and its role in geologic carbon storage. *Surf. Process Transp. Storage* **2023**, *4*, 423–477.
9. Mathieu, P. CO_2 Emissions Mitigation from Power Generation Using Capture Technologies. In *Sustainable Energy Technologies: Options and Prospects*; Springer: Dordrecht, The Netherlands, 2008; pp. 195–205. Available online: https://link.springer.com/chapter/10.1007/978-1-4020-6724-2_10 (accessed on 25 June 2024).
10. IEA. The Role of CO_2 Storage—Analysis. Available online: https://www.iea.org/reports/the-role-of-co2-storage (accessed on 1 October 2024).
11. Liu, Y.; Ren, G.; Shen, H.; Liu, G.; Li, F. Technology of CO_2 capture and storage. *E3S Web Conf.* **2019**, *118*, 01046. [CrossRef]
12. Cozzi, P.G.; Gualandi, A.; Potenti, S.; Calogero, F.; Rodeghiero, G. Asymmetric Reactions Enabled by Cooperative Enantioselective Amino- and Lewis Acid Catalysis. In *Asymmetric Organocatalysis Combined with Metal Catalysis*; Topics in Current Chemistry Collections; Springer: Cham, Switzerland, 2020; pp. 29–65.
13. Kelemen, P.; Benson, S.M.; Pilorgé, H.; Psarras, P.; Wilcox, J. An Overview of the Status and Challenges of CO_2 Storage in Minerals and Geological Formations. *Front. Clim.* **2019**, *1*, 482595. [CrossRef]
14. Xu, S.; Baslaib, M.; Keebali, A.; Para, H.; BinAmro, A. Potential for Permanent CO_2 Geological Storage, an Onshore Abu Dhabi Large Scale Assessment. In Proceedings of the Society of Petroleum Engineers-ADIPEC 2022, Abu Dhabi, United Arab Emirates, 31 October–3 November 2022.
15. Albertz, M.; Stewart, S.A.; Goteti, R. Perspectives on geologic carbon storage. *Front. Energy Res.* **2022**, *10*, 1071735. [CrossRef]

16. Pearce, J.; Raza, S.; Baublys, K.; Hayes, P.; Firouzi, M.; Rudolph, V. Unconventional CO_2 Storage: CO_2 Mineral Trapping Predicted in Characterized Shales, Sandstones, and Coal Seam Interburden. *SPE J.* **2022**, *27*, 3218–3239. [CrossRef]
17. Lai, X.; Chen, X.; Wang, Y.; Dai, D.; Dong, J.; Liu, W. Feasibility Analyses and Prospects of CO_2 Geological Storage by Using Abandoned Shale Gas Wells in the Sichuan Basin, China. *Atmosphere* **2022**, *13*, 1698. [CrossRef]
18. Garcia, S.; Kaminska, A.; Maroto-Valer, M.M. Underground carbon dioxide storage in saline formations. *Proc. Inst. Civ. Eng. Waste Resour. Manag.* **2010**, *163*, 77–88. [CrossRef]
19. Wang, B.; Wang, X.; Chen, Y.; Liang, Q.; Zeng, F. A Review-Dissolution and Mineralization Storage of CO_2 Geological Storage in Saline Aquifers. In Proceedings of the SPE Canadian Energy Technology Conference and Exhibition, Calgary, AL, Canada, 15–16 March 2023; pp. 15–16. Available online: http://onepetro.org/specet/proceedings-pdf/23CET/1-23CET/D012S008R001/3089094/spe-212790-ms.pdf/1 (accessed on 3 June 2024).
20. De Silva, G.P.D.; Ranjith, P.G.; Perera, M.S.A. Geochemical aspects of CO_2 sequestration in deep saline aquifers: A review. *Fuel* **2015**, *155*, 128–143. [CrossRef]
21. Khandoozi, S.; Hazlett, R.; Fustic, M. A critical review of CO_2 mineral trapping in sedimentary reservoirs–from theory to application: Pertinent parameters, acceleration methods and evaluation workflow. *Earth-Sci. Rev.* **2023**, *244*, 104515. [CrossRef]
22. Jun, Y.S.; Giammar, D.E.; Werth, C.J. Impacts of geochemical reactions on geologic carbon sequestration. *Environ. Sci. Technol.* **2013**, *47*, 3–8. [CrossRef]
23. Montegrossi, G.; Cantucci, B.; Piochi, M.; Fusi, L.; Misnan, M.S.; Rashidi, M.R.A.; Abu Bakar, Z.A.; Tuan Harith, Z.Z.; Bahri, N.H.S.; Hashim, N. CO_2 Reaction-Diffusion Experiments in Shales and Carbonates. *Minerals* **2023**, *13*, 56. [CrossRef]
24. Zaidin, M.F.; Razak, A.A.; Amin, S.M.; Mohsin, N.; Pin, Y.W.; Tewari, R.D. Geochemistry Study for the CO_2-H_2S Injection for Storage: Experimental and Modelling. In Proceedings of the SPE Annual Technical Conference and Exhibition, San Antonio, TX, USA, 16–18 October 2023; Society of Petroleum Engineers (SPE): Richardson, TX, USA, 2023.
25. Lu, J.; Kharaka, Y.K.; Thordsen, J.J.; Horita, J.; Karamalidis, A.; Griffith, C.; Hakala, J.A.; Ambats, G.; Cole, D.R.; Phelps, T.J.; et al. CO_2-rock-brine interactions in Lower Tuscaloosa Formation at Cranfield CO_2 sequestration site, Mississippi, U.S.A. *Chem. Geol.* **2012**, *291*, 269–277. [CrossRef]
26. Kharaka, Y.K.; Cole, D.R.; Thordsen, J.J.; Gans, K.D.; Thomas, R.B. Geochemical Monitoring for Potential Environmental Impacts of Geologic Sequestration of CO_2. *Rev. Mineral. Geochem.* **2013**, *77*, 399–430. [CrossRef]
27. Khan, M.N.; Siddiqui, S.; Thakur, G.C. Recent Advances in Geochemical and Mineralogical Studies on CO_2–Brine–Rock Interaction for CO_2 Sequestration: Laboratory and Simulation Studies. *Energies* **2024**, *17*, 3346. [CrossRef]
28. Wang, J.; Wang, H.; Wang, X.; Yang, S.; Wu, H.; Leung, C.; Tian, J. A multiphysical-geochemical coupling model for caprock sealing efficiency in CO_2 geosequestration. *Deep. Undergr. Sci. Eng.* **2023**, *2*, 188–203. [CrossRef]
29. Zhang, C.; Wang, Y.; Kou, Z.; Zhang, L. Recent research advances in enhanced CO_2 mineralization and geologic CO_2 storage. *Adv. Geo-Energy Res.* **2023**, *10*, 141–145. [CrossRef]
30. Espinoza, D.N.; Santamarina, J.C. Water-CO_2-mineral systems: Interfacial tension, contact angle, and diffusion—Implications to CO_2 geological storage. *Water Resour. Res.* **2010**, *46*, 7537. [CrossRef]
31. Hajiabadi, S.H.; Bedrikovetsky, P.; Borazjani, S.; Mahani, H. Well Injectivity during CO_2 Geosequestration: A Review of Hydro-Physical, Chemical, and Geomechanical Effects. *Energy Fuels* **2021**, *35*, 9240–9267. [CrossRef]
32. Ren, L.; Liu, Q.; Ni, Y.; Xia, Y.; Chen, J. Study on the Ways to Improve the CO_2-H_2O Displacement Efficiency in Heterogeneous Porous Media by Lattice Boltzmann Simulation. *ACS Omega* **2022**, *7*, 20833–20844. [CrossRef] [PubMed]
33. Lacis, A.A.; Schmidt, G.A.; Rind, D.; Ruedy, R.A. Atmospheric CO_2: Principal control knob governing earth's temperature. *Science* **2010**, *330*, 356–359. [CrossRef]
34. Gaurina-Međimurec, N. The Influence of CO_2 on Well Cement. Available online: https://www.researchgate.net/publication/49600704 (accessed on 10 July 2024).
35. CO2CRC—Building a Low Emissions Future. Available online: https://co2crc.com.au/ (accessed on 26 June 2024).
36. Kharaka, Y.K.; Cole, D.R. Geochemistry of Geologic Sequestration of Carbon Dioxide. In *Frontiers in Geochemistry: Contribution of Geochemistry to the Study of the Earth*; John Wiley and Sons: Hoboken, NJ, USA, 2011; pp. 133–174.
37. Depaolo, D.J.; Cole, D.R. Geochemistry of Geologic Carbon Sequestration: An Overview. *Rev. Mineral. Geochem.* **2013**, *77*, 1–14. [CrossRef]
38. Bashir, A.; Ali, M.; Patil, S.; Aljawad, M.S.; Mahmoud, M.; Al-Shehri, D.; Hoteit, H.; Kamal, M.S. Comprehensive review of CO_2 geological storage: Exploring principles, mechanisms, and prospects. *Earth-Sci. Rev.* **2024**, *249*, 104672. [CrossRef]
39. Chiquet, P.; Daridon, J.L.; Broseta, D.; Thibeau, S. CO_2/water interfacial tensions under pressure and temperature conditions of CO_2 geological storage. *Energy Convers. Manag.* **2007**, *48*, 736–744. [CrossRef]
40. Benson, S.M.; Cole, D.R. CO_2 Sequestration in Deep Sedimentary Formations. *Elements* **2008**, *4*, 325–331. [CrossRef]
41. Bachu, S. Sequestration of CO_2 in geological media in response to climate change: Road map for site selection using the transform of the geological space into the CO_2 phase space. *Energy Convers. Manag.* **2002**, *43*, 87–102. [CrossRef]
42. Zhu, D.; Peng, S.; Zhao, S.; Wei, M.; Bai, B. Comprehensive Review of Sealant Materials for Leakage Remediation Technology in Geological CO_2 Capture and Storage Process. *Energy Fuels* **2021**, *35*, 4711–4742. [CrossRef]
43. Bachu, S. CO_2 storage in geological media: Role, means, status and barriers to deployment. *Prog. Energy Combust. Sci.* **2008**, *34*, 254–273. [CrossRef]

44. Celia, M.A.; Nordbotten, J.M. Practical Modeling Approaches for Geological Storage of Carbon Dioxide. *Groundwater* **2009**, *47*, 627–638. [CrossRef] [PubMed]
45. Witkowski, A.; Majkut, M.; Rulik, S. Analysis of pipeline transportation systems for carbon dioxide sequestration. *Arch. Thermodyn.* **2014**, *35*, 117–140. [CrossRef]
46. Juanes, R.; Spiteri, E.J.; Orr, F.M.; Blunt, M.J. Impact of relative permeability hysteresis on geological CO_2 storage. *Water Resour. Res.* **2006**, *42*, W12418. [CrossRef]
47. Massarweh, O.; Abushaikha, A.S. CO_2 sequestration in subsurface geological formations: A review of trapping mechanisms and monitoring techniques. *Earth-Sci. Rev.* **2024**, *253*, 104793. [CrossRef]
48. Altman, S.J.; Aminzadeh, B.; Balhoff, M.T.; Bennett, P.C.; Bryant, S.L.; Cardenas, M.B.; Chaudhary, K.; Cygan, R.T.; Deng, W.; Dewers, T.; et al. Chemical and hydrodynamic mechanisms for long-term geological carbon storage. *J. Phys. Chem. C* **2014**, *118*, 15103–15113. [CrossRef]
49. MousaviMirkalaei, S.M.; Edmondson, M.D. Coupled Geochemistry CCS Modelling: How Much Simplification is Required? In Proceedings of the Offshore Technology Conference Asia, Kuala Lumpur, Malaysia, 27 February–1 March 2024.
50. Emami-Meybodi, H.; Hassanzadeh, H.; Green, C.P.; Ennis-King, J. Convective dissolution of CO_2 in saline aquifers: Progress in modeling and experiments. *Int. J. Greenh. Gas Control.* **2015**, *40*, 238–266. [CrossRef]
51. Ajayi, T.; Gomes, J.S.; Bera, A. A review of CO_2 storage in geological formations emphasizing modeling, monitoring and capacity estimation approaches. *Pet. Sci.* **2019**, *16*, 1028–1063. [CrossRef]
52. Cao, C.; Liu, H.; Hou, Z.; Mehmood, F.; Liao, J.; Feng, W. A review of CO_2 storage in view of safety and cost-effectiveness. *Energies* **2020**, *13*, 600. [CrossRef]
53. Yang, F.; Bai, B.; Tang, D.; Shari, D.N.; David, W. Characteristics of CO_2 sequestration in saline aquifers. *Pet. Sci.* **2009**, *7*, 83–92. [CrossRef]
54. Bickle, M.; Kampman, N.; Wigley, M. Natural Analogues. *Rev. Mineral. Geochem.* **2013**, *77*, 15–71. [CrossRef]
55. Kampman, N.; Bickle, M.; Wigley, M.; Dubacq, B. Fluid flow and CO_2-fluid-mineral interactions during CO_2-storage in sedimentary basins. *Chem. Geol.* **2014**, *369*, 22–50. [CrossRef]
56. Xu, T.; Apps, J.A.; Pruess, K. Analysis of Mineral Trapping for CO_2 Disposal in Deep Aquifers. 2001. Available online: https://escholarship.org/uc/item/59c8k6gb (accessed on 24 June 2024).
57. Xu, T.; Apps, J.A.; Pruess, K. Reactive geochemical transport simulation to study mineral trapping for CO_2 disposal in deep arenaceous formations. *J. Geophys. Res. Solid Earth* **2003**, *108*, 2071. [CrossRef]
58. Iglauer, S.; Al-Yaseri, A.Z.; Rezaee, R.; Lebedev, M. CO_2 wettability of caprocks: Implications for structural storage capacity and containment security. *Geophys. Res. Lett.* **2015**, *42*, 9279–9284. [CrossRef]
59. Arif, M.; Barifcani, A.; Lebedev, M.; Iglauer, S. Structural trapping capacity of oil-wet caprock as a function of pressure, temperature and salinity. *Int. J. Greenh. Gas Control* **2016**, *50*, 112–120. [CrossRef]
60. Ali, M.; Aftab, A.; Arain, Z.U.A.; Al-Yaseri, A.; Roshan, H.; Saeedi, A.; Iglauer, S.; Sarmadivaleh, M. Influence of Organic Acid Concentration on Wettability Alteration of Cap-Rock: Implications for CO_2 Trapping/Storage. *ACS Appl. Mater. Interfaces* **2020**, *12*, 39850–39858. [CrossRef]
61. Ali, M.; Awan, F.U.R.; Ali, M.; Al-Yaseri, A.; Arif, M.; Sánchez-Román, M.; Keshavarz, A.; Iglauer, S. Effect of humic acid on CO_2-wettability in sandstone formation. *J. Colloid Interface Sci.* **2021**, *588*, 315–325. [CrossRef]
62. Iglauer, S. Dissolution Trapping of Carbon Dioxide in Reservoir Formation Brine—A Carbon Storage Mechanism. In *Mass Transfer-Advanced Aspects*; InTech: London, UK, 2011.
63. Pentland, C.H.; El-Maghraby, R.; Georgiadis, A.; Iglauer, S.; Blunt, M.J. Immiscible displacements and capillary trapping in CO_2 storage. *Energy Procedia* **2011**, *4*, 4969–4976. [CrossRef]
64. Golding, S.D.; Uysal, I.T.; Boreham, C.J.; Kirste, D.; Baublys, K.A.; Esterle, J.S. Adsorption and mineral trapping dominate CO_2 storage in coal systems. *Energy Procedia* **2011**, *4*, 3131–3138. [CrossRef]
65. Bachu, S.; Adams, J.J. Sequestration of CO_2 in geological media in response to climate change: Capacity of deep saline aquifers to sequester CO_2 in solution. *Energy Convers. Manag.* **2003**, *44*, 3151–3175. [CrossRef]
66. Kim, K.; Kim, D.; Na, Y.; Song, Y.; Wang, J. A review of carbon mineralization mechanism during geological CO_2 storage. *Heliyon* **2023**, *9*, e23135. [CrossRef] [PubMed]
67. Wen, G.; Benson, S.M. CO_2 plume migration and dissolution in layered reservoirs. *Int. J. Greenh. Gas Control* **2019**, *87*, 66–79. [CrossRef]
68. Li, W.; Nan, Y.; Zhang, Z.; You, Q.; Jin, Z. Hydrophilicity/hydrophobicity driven CO_2 solubility in kaolinite nanopores in relation to carbon sequestration. *Chem. Eng. J.* **2020**, *398*, 125449. [CrossRef]
69. Gutiérrez, F.; Lizaga, I. Sinkholes, collapse structures and large landslides in an active salt dome submerged by a reservoir: The unique case of the Ambal ridge in the Karun River, Zagros Mountains, Iran. *Geomorphology* **2016**, *254*, 88–103. [CrossRef]
70. Chang, Y.B.; Coats, B.K.; Nolen, J.S. A Compositional Model for CO_2 Floods Including CO_2 Solubility in Water. In Proceedings of the Society of Petroleum Engineers-Permian Basin Oil and Gas Recovery Conference, Midland, TX, USA, 27–29 March 1996; pp. 189–201. [CrossRef]
71. Bakhshian, S. Dynamics of dissolution trapping in geological carbon storage. *Int. J. Greenh. Gas Control* **2021**, *112*, 103520. [CrossRef]

72. Taheri, A.; Chen, Y.; Chen, S.; Li, D.; Jiang, X.; Kong-Macao, G.H. Density-Driven Convection for CO_2 Solubility Trapping in Saline Aquifers: Modeling and Influencing Factors. *Geotechnics* **2023**, *3*, 70–103. [CrossRef]
73. MacMinn, C.W.; Szulczewski, M.L.; Juanes, R. CO_2 migration in saline aquifers. Part 1. Capillary trapping under slope and groundwater flow. *J. Fluid Mech.* **2010**, *662*, 329–351. [CrossRef]
74. Eke, P.E.; Naylor, M.; Haszeldine, S.; Curtis, A. CO_2 Leakage Prevention Technologies. In Proceedings of the Society of Petroleum Engineers-Offshore Europe Oil and Gas Conference and Exhibition, Aberdeen, UK, 6–8 September 2011; pp. 207–220. [CrossRef]
75. Neufeld, J.A.; Hesse, M.A.; Riaz, A.; Hallworth, M.A.; Tchelepi, H.A.; Huppert, H.E. Convective dissolution of carbon dioxide in saline aquifers. *Geophys. Res. Lett.* **2010**, *37*, L22404. [CrossRef]
76. Sigfusson, B.; Gislason, S.R.; Matter, J.M.; Stute, M.; Gunnlaugsson, E.; Gunnarsson, I.; Aradottir, E.S.; Sigurdardottir, H.; Mesfin, K.; Alfredsson, H.A.; et al. Solving the carbon-dioxide buoyancy challenge: The design and field testing of a dissolved CO_2 injection system. *Int. J. Greenh. Gas Control* **2015**, *37*, 213–219. [CrossRef]
77. Addassi, M.; Omar, A.; Hoteit, H.; Afifi, A.M.; Arkadakskiy, S.; Ahmed, Z.T.; Kunnummal, N.; Gislason, S.R.; Oelkers, E.H. Assessing the potential of solubility trapping in unconfined aquifers for subsurface carbon storage. *Sci. Rep.* **2022**, *12*, 20452. [CrossRef]
78. Soong, Y.; Fauth, D.L.; Howard, B.H.; Jones, J.R.; Harrison, D.K.; Goodman, A.; Gray, M.L.; Frommell, E.A. CO_2 sequestration with brine solution and fly ashes. *Energy Convers. Manag.* **2006**, *47*, 1676–1685. [CrossRef]
79. Ali, M.; Jha, N.K.; Pal, N.; Keshavarz, A.; Hoteit, H.; Sarmadivaleh, M. Recent advances in carbon dioxide geological storage, experimental procedures, influencing parameters, and future outlook. *Earth-Sci. Rev.* **2022**, *225*, 103895. [CrossRef]
80. Pearce, J.K.; Dawson, G.K.W.; Sommacal, S.; Golding, S.D. Micro CT and experimental study of carbonate precipitation from CO_2 and produced water co-injection into sandstone. *Energies* **2021**, *14*, 6998. [CrossRef]
81. Steger, F.; Reich, J.; Fuchs, W.; Rittmann, S.K.M.; Gübitz, G.M.; Ribitsch, D.; Bochmann, G. Comparison of Carbonic Anhydrases for CO_2 Sequestration. *Int. J. Mol. Sci.* **2022**, *23*, 957. [CrossRef]
82. Power, I.M.; Harrison, A.L.; Dipple, G.M. Accelerating Mineral Carbonation Using Carbonic Anhydrase. *Environ. Sci. Technol.* **2016**, *50*, 2610–2618. [CrossRef]
83. Zheng, T.; Qian, C. Influencing factors and formation mechanism of $CaCO_3$ precipitation induced by microbial carbonic anhydrase. *Process Biochem.* **2020**, *91*, 271–281. [CrossRef]
84. Liu, B.; Mahmood, B.S.; Mohammadian, E.; Manshad, A.K.; Rosli, N.R.; Ostadhassan, M. Measurement of solubility of CO_2 in NaCl, $CaCl_2$, $MgCl_2$ and $MgCl_2$ + $CaCl_2$ brines at temperatures from 298 to 373 K and pressures up to 20 MPa using the potentiometric titration method. *Energies* **2021**, *14*, 7222. [CrossRef]
85. Cappuccio, J.A.; Pillar, V.D.; Xiao, C.; Yu, A.; Ajo-Franklin, C.M. Bacterially Acceleration of CaCO3 Mineralization. 2011. Available online: https://www.cell.com/biophysj/fulltext/S0006-3495(10)04360-2 (accessed on 9 June 2024).
86. Armstrong, R.; Ajo-Franklin, J. Investigating biomineralization using synchrotron based X-ray computed microtomography. *Geophys. Res. Lett.* **2011**, *38*, L08406. [CrossRef]
87. Hamm, L.M.; Bourg, I.C.; Wallace, A.F.; Rotenberg, B. Molecular Simulation of CO_2-and CO_3-Brine-Mineral Systems. *Rev. Mineral. Geochem.* **2013**, *77*, 189–228. [CrossRef]
88. Zhao, J.; Lu, W.; Zhang, F.; Lu, C.; Du, J.; Zhu, R.; Sun, L. Evaluation of CO_2 solubility-trapping and mineral-trapping in microbial-mediated CO_2–brine–sandstone interaction. *Mar. Pollut. Bull.* **2014**, *85*, 78–85. [CrossRef]
89. Zhang, R.; Winterfeld, P.H.; Yin, X.; Xiong, Y.; Wu, Y.S. Sequentially coupled THMC model for CO_2 geological sequestration into a 2D heterogeneous saline aquifer. *J. Nat. Gas Sci. Eng.* **2015**, *27*, 579–615. [CrossRef]
90. Zhang, C.P.; Cheng, P.; Ma, Z.Y.; Ranjith, P.G.; Zhou, J.P. Comparison of fracturing unconventional gas reservoirs using CO_2 and water: An experimental study. *J. Pet. Sci. Eng.* **2021**, *203*, 108598. [CrossRef]
91. Gislason, S.R.; Wolff-Boenisch, D.; Stefansson, A.; Oelkers, E.H.; Gunnlaugsson, E.; Sigurdardottir, H.; Sigfusson, B.; Broecker, W.S.; Matter, J.M.; Stute, M.; et al. Mineral sequestration of carbon dioxide in basalt: A pre-injection overview of the CarbFix project. *Int. J. Greenh. Gas Control* **2010**, *4*, 537–545. [CrossRef]
92. Ali, M.; Arif, M.; Sahito, M.F.; Al-Anssari, S.; Keshavarz, A.; Barifcani, A.; Stalker, L.; Sarmadivaleh, M.; Iglauer, S. CO_2-wettability of sandstones exposed to traces of organic acids: Implications for CO_2 geo-storage. *Int. J. Greenh. Gas Control* **2019**, *83*, 61–68. [CrossRef]
93. Iglauer, S.; Pentland, C.H.; Busch, A. CO_2 wettability of seal and reservoir rocks and the implications for carbon geo-sequestration. *Water Resour. Res.* **2015**, *51*, 729–774. [CrossRef]
94. Ruprecht, C.; Pini, R.; Falta, R.; Benson, S.; Murdoch, L. Hysteretic trapping and relative permeability of CO_2 in sandstone at reservoir conditions. *Int. J. Greenh. Gas Control* **2014**, *27*, 15–27. [CrossRef]
95. Rahman, T.; Lebedev, M.; Barifcani, A.; Iglauer, S. Residual trapping of supercritical CO_2 in oil-wet sandstone. *J. Colloid Interface Sci.* **2016**, *469*, 63–68. [CrossRef]
96. Burnside, N.M.; Naylor, M. Review and implications of relative permeability of CO_2/brine systems and residual trapping of CO_2. *Int. J. Greenh. Gas Control* **2014**, *23*, 1–11. [CrossRef]
97. Lamy, C.; Tech, P.; Iglauer, S.; Pentland, C.H.; Blunt, M.J.; Maitland, G. SPE 130720 Capillary Trapping in Carbonate Rocks. 2010. Available online: https://onepetro.org/SPEEURO/proceedings-abstract/10EURO/10EURO/SPE-130720-MS/106132 (accessed on 20 June 2024).

98. Zhang, H.; Arif, M. Residual trapping capacity of subsurface systems for geological storage of CO_2: Measurement techniques, meta-analysis of influencing factors, and future outlook. *Earth-Sci. Rev.* **2024**, *252*, 104764. [CrossRef]
99. Rezk, M.G.; Foroozesh, J.; Zivar, D.; Mumtaz, M. CO_2 storage potential during CO_2 enhanced oil recovery in sandstone reservoirs. *J. Nat. Gas Sci. Eng.* **2019**, *66*, 233–243. [CrossRef]
100. Ang, L.; Yongming, L.; Xi, C.; Zhongyi, Z.; Yu, P. Review of CO_2 sequestration mechanism in saline aquifers. *Nat. Gas Ind. B* **2022**, *9*, 383–393.
101. Zhang, D.; Song, J. Mechanisms for geological carbon sequestration. *Procedia IUTAm* **2014**, *10*, 319–327. [CrossRef]
102. Vishal, V.; Singh, T.N. Geologic carbon sequestration: Understanding reservoir behavior. In *Geologic Carbon Sequestration: Understanding Reservoir Behavior*; Springer: Cham, Switzerland, 2016; pp. 1–338.
103. Song, J.; Zhang, D. Comprehensive review of caprock-sealing mechanisms for geologic carbon sequestration. *Environ. Sci. Technol.* **2013**, *47*, 9–22. [CrossRef] [PubMed]
104. Ampomah, W.; Balch, R.; Cather, M.; Rose-Coss, D.; Dai, Z.; Heath, J.; Dewers, T.; Mozley, P. Evaluation of CO_2 Storage Mechanisms in CO_2 Enhanced Oil Recovery Sites: Application to Morrow Sandstone Reservoir. *Energy Fuels* **2016**, *30*, 8545–8555. [CrossRef]
105. Power, I.M.; Harrison, A.L.; Dipple, G.M.; Wilson, S.; Kelemen, P.B.; Hitch, M.; Southam, G. Carbon Mineralization: From Natural Analogues to Engineered Systems. *Rev. Mineral. Geochem.* **2013**, *77*, 305–360. [CrossRef]
106. Sanna, A.; Uibu, M.; Caramanna, G.; Kuusik, R.; Maroto-Valer, M.M. A review of mineral carbonation technologies to sequester CO_2. *Chem. Soc. Rev.* **2014**, *43*, 8049. [CrossRef]
107. Assima, G.P.; Larachi, F.; Molson, J.; Beaudoin, G. Impact of temperature and oxygen availability on the dynamics of ambient CO_2 mineral sequestration by nickel mining residues. *Chem. Eng. J.* **2014**, *240*, 394–403. [CrossRef]
108. Aminu, M.D.; Nabavi, S.A.; Rochelle, C.A.; Manovic, V. A review of developments in carbon dioxide storage. *Appl. Energy* **2017**, *208*, 1389–1419. [CrossRef]
109. Li, W.; Nan, Y.; You, Q.; Jin, Z. CO_2 solubility in brine in silica nanopores in relation to geological CO_2 sequestration in tight formations: Effect of salinity and pH. *Chem. Eng. J.* **2021**, *411*, 127626. [CrossRef]
110. Palandri, J.L.; Kharaka, Y.K. A Compilation of Rate Parameters of Water-Mineral Interaction Kinetics for Application to Geochemical Modeling. Open-File Report. 2004. Available online: https://pubs.usgs.gov/of/2004/1068/pdf/OFR_2004_1068.pdf (accessed on 17 June 2024).
111. Fitts, J.P.; Peters, C.A. Caprock Fracture Dissolution and CO_2 Leakage. *Rev. Mineral. Geochem.* **2013**, *77*, 459–479. [CrossRef]
112. Hesjevik, S.M.; Olsen, S.; Arkitekt, S.; Trondheim, E.V.; Seiersten, M. Corrosion at High CO_2 Pressure. 10 N-7005. Available online: http://onepetro.org/NACECORR/proceedings-pdf/CORR03/All-CORR03/NACE-03345/1877132/nace-03345.pdf/1 (accessed on 31 May 2024).
113. Gaus, I.; Audigane, P.; André, L.; Lions, J.; Jacquemet, N.; Durst, P.; Czernichowski-Lauriol, I.; Azaroual, M. Geochemical and solute transport modelling for CO_2 storage, what to expect from it? *Int. J. Greenh. Gas Control* **2008**, *2*, 605–625. [CrossRef]
114. Luo, C.; Liu, H.Q.; Wang, Z.C.; Lyu, X.C.; Zhang, Y.Q.; Zhou, S. A comprehensive study on the effect of rock corrosion and CO_2 on oil-water interfacial tension during CO_2 injection in heavy oil reservoirs. *Pet. Sci. Technol.* **2023**, 1–13. [CrossRef]
115. Raza, A.; Gholami, R.; Sarmadivaleh, M.; Tarom, N.; Rezaee, R.; Bing, C.H.; Nagarajan, R.; Hamid, M.A.; Elochukwu, H. Integrity analysis of CO_2 storage sites concerning geochemical-geomechanical interactions in saline aquifers. *J. Nat. Gas Sci. Eng.* **2016**, *36*, 224–240. [CrossRef]
116. Liu, E.; Lu, X.; Wang, D. A Systematic Review of Carbon Capture, Utilization and Storage: Status, Progress and Challenges. *Energies* **2023**, *16*, 2865. [CrossRef]
117. Cheng, Q.; Tang, J.; Liu, Y.; Jia, Y.; Lu, Y.; Sun, X.; Zhao, G.; Liu, Y. Pore alteration of Yanchang shale after CO_2-brine-rock interaction: Influence on the integrity of caprock in CO_2 geological sequestration. *Fuel* **2024**, *363*, 130952. [CrossRef]
118. Rohmer, J.; Pluymakers, A.; Renard, F. Mechano-chemical interactions in sedimentary rocks in the context of CO_2 storage: Weak acid, weak effects? *Earth-Sci. Rev.* **2016**, *157*, 86–110. [CrossRef]
119. Zhou, J.; Yang, K.; Zhou, L.; Jiang, Y.; Xian, X.; Zhang, C.; Tian, S.; Fan, M.; Lu, Z. Microstructure and mechanical properties alterations in shale treated via CO_2/CO_2-water exposure. *J. Pet. Sci. Eng.* **2021**, *196*, 108088. [CrossRef]
120. Md Yusof, M.A.; Mohamed, M.A.; Md Akhir, N.A.; Ibrahim, M.A.; Saaid, I.M.; Idris, A.K.; Idress, M.; Awangku Matali, A.A.A. Influence of Brine–Rock Parameters on Rock Physical Changes During CO_2 Sequestration in Saline Aquifer. *Arab. J. Sci. Eng.* **2022**, *47*, 11345–11359. [CrossRef]
121. Adila, A.S.; Raza, A.; Zhang, Y.; Mahmoud, M.; Arif, M. Geochemical Interactions Among Rock/CO_2/Brine Systems: Implications for CO_2 Geo-Storage. In Proceedings of the Society of Petroleum Engineers-Gas and Oil Technology Showcase and Conference, GOTS 2023, Dubai, United Arab Emirates, 13–15 March 2023. [CrossRef]
122. Li, Z.; Lv, Y.; Liu, B.; Fu, X. Reactive Transport Modeling of CO_2-Brine–Rock Interaction on Long-Term CO_2 Sequestration in Shihezi Formation. *Energies* **2023**, *16*, 670. [CrossRef]
123. Soong, Y.; Howard, B.; Haljasmaa, I.; Crandall, D.; Dilmore, R.; Dalton, L.E.; Wu, Z.; Wang, P.; Gray, M.L.; Shi, F. CO_2/Brine/Rock Interactions in the Cedar Keys-Lawson Formation. *Univers. J. Carbon Res.* **2023**, *1*, 48–62. [CrossRef]
124. Qiu, R.; Zhang, G.; Anhai, Z.; Mingjing, L.; Feng, Y.; Zhou, D. Effects of Supercritical CO_2-Brine/shale Interaction on Fracturing Behavior. In Proceedings of the 57th US Rock Mechanics/Geomechanics Symposium, Atlanta, GA, USA, 25–28 June 2023. [CrossRef]

125. Li, S.; Zhang, S.; Xing, H.; Zou, Y. CO_2–brine–rock interactions altering the mineralogical, physical, and mechanical properties of carbonate-rich shale oil reservoirs. *Energy* **2022**, *256*, 124608. [CrossRef]
126. Arous, S.J.A.; Tehrani, D.M.; Bazvand, M. Investigation of the effects of carbon dioxide injection on the rock and fluid intraction in high permeable sandstone reserviors. *Pet. Sci. Technol.* **2023**, *41*, 387–405. [CrossRef]
127. Føyen, T.; Brattekås, B.; Fernø, M.A.; Barrabino, A.; Holt, T. Increased CO_2 storage capacity using CO_2-foam. *Int. J. Greenh. Gas Control* **2020**, *96*, 103016. [CrossRef]
128. Sæle, A.M.; Graue, A.; Alcorn, Z.P. The Effect of Rock Type on CO_2 Foam for CO_2 EOR and CO_2 Storage. In Proceedings of the International Petroleum Technology Conference, Bangkok, Thailand, 1–3 March 2023. [CrossRef]
129. Rezaee, R.; Saeedi, A.; Iglauer, S.; Evans, B. Shale alteration after exposure to supercritical CO_2. *Int. J. Greenh. Gas Control* **2017**, *62*, 91–99. [CrossRef]
130. Qin, C.; Jiang, Y.; Luo, Y.; Xian, X.; Liu, H.; Li, Y. Effect of supercritical carbon dioxide treatment time, pressure, and temperature on shale water wettability. *Energy Fuels* **2017**, *31*, 493–503. [CrossRef]
131. Lu, Y.; Gong, T.; Tang, J.; Cheng, Q.; Zhang, C.; Zhao, G.; Liu, B. Evolution of shale wetting properties under long-term CO_2/brine/shale interaction: Implications for CO_2 storage in shale reservoirs. *Gas Sci. Eng.* **2024**, *126*, 205334. [CrossRef]
132. Liu, Q.; Mercedes Maroto-Valer, M. Parameters affecting mineral trapping of CO_2 sequestration in brines. *Greenh. Gases Sci. Technol.* **2011**, *1*, 211–222. [CrossRef]
133. Shi, Y.; Lu, Y.; Rong, Y.; Bai, Z.; Bai, H.; Li, M.; Zhang, Q. Geochemical reaction of compressed CO_2 energy storage using saline aquifer. *Alex. Eng. J.* **2023**, *64*, 679–689. [CrossRef]
134. Vafaie, A.; Cama, J.; Soler, J.M.; Kivi, I.R.; Vilarrasa, V. Chemo-hydro-mechanical effects of CO_2 injection on reservoir and seal rocks: A review on laboratory experiments. *Renew. Sustain. Energy Rev.* **2023**, *178*, 113270. [CrossRef]
135. Liu, Q.; Zhu, D.; Jin, Z.; Tian, H.; Zhou, B.; Jiang, P.; Meng, Q.; Wu, X.; Xu, H.; Hu, T.; et al. Carbon capture and storage for long-term and safe sealing with constrained natural CO_2 analogs. *Renew. Sustain. Energy Rev.* **2023**, *171*, 113000. [CrossRef]
136. Zaidin, M.F.; Amin, S.M.; Azuddin, F.J.; Razak, A.A.; Mohsin, N.; Pin, Y.W.; Tewari, R.D. Enhancing CO_2-H_2S Storage Predictions in High H_2S Fields: Improving Model Accuracy and Kinetic Rate Information. In Proceedings of the International Petroleum Technology Conference, Dhahran, Saudi Arabia, 12 February 2024.
137. Hazarika, S.; Boruah, A.; Kumar, H. Study of pore structure of shale formation for CO_2 storage. *Mater. Today Proc.* **2023**. [CrossRef]
138. Jha, N.K.; Ali, M.; Sarmadivaleh, M.; Iglauer, S.; Barifcani, A.; Lebedev, M.; Sangwai, J. Low Salinity Surfactant Nanofluids for Enhanced CO_2 Storage Application At High Pressure and Temperature. In Proceedings of the The Netherlands Fifth CO_2 Geological Storage Workshop, Utrecht, The Netherlands, 21–23 November 2018.
139. Ali, M.; Sahito, M.F.; Jha, N.K.; Memon, S.; Keshavarz, A.; Iglauer, S.; Saeedi, A.; Sarmadivaleh, M. Effect of nanofluid on CO_2-wettability reversal of sandstone formation; implications for CO_2 geo-storage. *J. Colloid Interface Sci.* **2020**, *559*, 304–312. [CrossRef] [PubMed]
140. Wang, K.; Xu, T.; Wang, F.; Tian, H. Experimental study of CO_2–brine–rock interaction during CO_2 sequestration in deep coal seams. *Int. J. Coal Geol.* **2016**, *154–155*, 265–274. [CrossRef]
141. Mohamed, I.M.; Nasr-El-Din, H.A. Fluid/rock interactions during CO_2 sequestration in deep saline carbonate aquifers: Laboratory and modeling studies. *SPE J.* **2013**, *18*, 468–485. [CrossRef]
142. Palencia, C.; Araujo De Itriago, Y.; Singletary, P. Potential Damage Complications in Supercritical CO_2 Storage. 2023. Available online: http://onepetro.org/urtecla/proceedings-pdf/23JLAU/1-23JLAU/D011S001R003/3383030/urtec-2023-3969779-ms.pdf (accessed on 8 July 2024).
143. Shukla, R.; Ranjith, P.; Haque, A.; Choi, X. A review of studies on CO_2 sequestration and caprock integrity. *Fuel* **2010**, *89*, 2651–2664. [CrossRef]
144. Lu, J.; Partin, J.W.; Hovorka, S.D.; Wong, C. Potential risks to freshwater resources as a result of leakage from CO_2 geological storage: A batch-reaction experiment. *Environ. Earth Sci.* **2010**, *60*, 335–348. [CrossRef]
145. Little, M.G.; Jackson, R.B. Potential impacts of leakage from deep CO_2 geosequestration on overlying freshwater aquifers. *Environ. Sci. Technol.* **2010**, *44*, 9225–9232. [CrossRef]
146. Espinoza, D.N.; Santamarina, J.C. CO_2 breakthrough—Caprock sealing efficiency and integrity for carbon geological storage. *Int. J. Greenh. Gas Control* **2017**, *66*, 218–229. [CrossRef]
147. Kaldi, J.; Daniel, R.; Tenthorey, E.; Michael, K.; Schacht, U.; Nicol, A.; Underschultz, J.; Backe, G. Containment of CO_2 in CCS: Role of Caprocks and Faults. *Energy Procedia* **2013**, *37*, 5403–5410. [CrossRef]
148. Song, Y.; Jun, S.; Na, Y.; Kim, K.; Jang, Y.; Wang, J. Geomechanical challenges during geological CO_2 storage: A review. *Chem. Eng. J.* **2023**, *456*, 140968. [CrossRef]
149. Gillioz, A.; Verga, F.; Deangeli, C. Critical Parameters for Caprock Tensile Failure Induced by CO_2 Injection into Aquifers. In Proceedings of the SPE Europe Energy Conference and Exhibition, Turin, Italy, 26–28 June 2024; pp. 26–28. [CrossRef]
150. de Kok, J. Monitoring Injectivity for CO_2 Injection in Depleted Gas Reservoirs. In Proceedings of the SPE Europe Energy Conference and Exhibition, Turin, Italy, 26–28 June 2024. [CrossRef]
151. Khan, S.; Khulief, Y.; Al-Shuhail, A.; Bashmal, S.; Iqbal, N. The Geomechanical and Fault Activation Modeling during CO_2 Injection into Deep Minjur Reservoir, Eastern Saudi Arabia. *Sustainability* **2020**, *12*, 9800. [CrossRef]
152. Celia, M.A.; Nordbotten, J.M.; Court, B.; Dobossy, M.; Bachu, S. Field-scale application of a semi-analytical model for estimation of CO_2 and brine leakage along old wells. *Int. J. Greenh. Gas Control* **2011**, *5*, 257–269. [CrossRef]

153. Birkholzer, J.T.; Nicot, J.P.; Oldenburg, C.M.; Zhou, Q.; Kraemer, S.; Bandilla, K. Brine flow up a well caused by pressure perturbation from geologic carbon sequestration: Static and dynamic evaluations. *Int. J. Greenh. Gas Control* **2011**, *5*, 850–861. [CrossRef]
154. Gholami, R.; Raza, A.; Iglauer, S. Leakage risk assessment of a CO_2 storage site: A review. *Earth-Sci. Rev.* **2021**, *223*, 103849. [CrossRef]
155. Carey, J.W. Geochemistry of Wellbore Integrity in CO_2 Sequestration: Portland Cement-Steel-Brine-CO_2 Interactions. *Rev. Mineral. Geochem.* **2013**, *77*, 505–539. [CrossRef]
156. Nordboiten, J.M.; Kavetski, D.; Celia, M.A.; Bachu, S. Model for CO_2 leakage including multiple geological layers and multiple leaky wells. *Environ. Sci. Technol.* **2009**, *43*, 743–749. [CrossRef]
157. Viswanathan, H.S.; Pawar, R.J.; Stauffer, P.H.; Kaszuba, J.P.; Carey, J.W.; Olsen, S.C.; Keating, G.N.; Kavetski, D.; Guthrie, G.D. Development of a hybrid process and system model for the assessment of wellbore leakage at a geologic CO_2 sequestration site. *Environ. Sci. Technol.* **2008**, *42*, 7280–7286. [CrossRef]
158. Feng, Y.; Yan, W.; Zhang, L.; Wang, Y. Corrosion in CO_2 Geological Utilization and Storage. In *Corrosion in CO_2 Capture, Transportation, Geological Utilization and Storage*; Engineering Materials; Springer: Singapore, 2023; Part F680; pp. 47–79. Available online: https://link.springer.com/chapter/10.1007/978-981-99-2392-2_4 (accessed on 7 August 2024).
159. Su, X.; Liu, S.; Zhang, L.; Liu, G.; Wang, Y.; Gan, M.; Li, X. Wellbore leakage risk management in CO_2 geological utilization and storage: A review. *Energy Rev.* **2023**, *2*, 100049. [CrossRef]
160. Raza, A.; Gholami, R.; Rabiei, M.; Rasouli, V.; Rezaee, R.; Fakhari, N. Impact of geochemical and geomechanical changes on CO_2 sequestration potential in sandstone and limestone aquifers. *Greenh. Gases Sci. Technol.* **2019**, *9*, 905–923. [CrossRef]
161. Emberley, S.; Hutcheon, I.; Shevalier, M.; Durocher, K.; Gunter, W.D.; Perkins, E.H. Geochemical monitoring of fluid-rock interaction and CO_2 storage at the Weyburn CO_2-injection enhanced oil recovery site, Saskatchewan, Canada. *Energy* **2004**, *29*, 1393–1401. [CrossRef]
162. Busch, A.; Bertier, P.; Gensterblum, Y.; Rother, G.; Spiers, C.J.; Zhang, M.; Wentinck, H.M. On sorption and swelling of CO_2 in clays. *Geomech. Geophys. Geo-Energy Geo-Resour.* **2016**, *2*, 111–130. [CrossRef]
163. Rutqvist, J. The geomechanics of CO_2 storage in deep sedimentary formations. *Geotech. Geol. Eng.* **2012**, *30*, 525–551. [CrossRef]
164. Shaffer, G. Long-term effectiveness and consequences of carbon dioxide sequestration. *Nat. Geosci.* **2010**, *3*, 464–467. [CrossRef]
165. Harvey, O.R.; Qafoku, N.P.; Cantrell, K.J.; Lee, G.; Amonette, J.E.; Brown, C.F. Geochemical Implications of Gas Leakage associated with Geologic CO_2 Storage—A Qualitative Review. *Environ. Sci. Technol.* **2012**, *47*, 23–36. [CrossRef] [PubMed]
166. Deel, D.; Mahajan, K.; Mahoney, C.R.; Mcilvried, H.G.; Srivastava, R.D. Risk Assessment and Management for Long-Term Storage of CO_2 in Geologic Formations-United States Department of Energy R&D. *Syst. Cybern. Inform.* **2007**, *5*, 79–84.
167. Raziperchikolaee, S.; Pasumarti, A. The impact of the depth-dependence of in-situ stresses on the effectiveness of stacked caprock reservoir systems for CO_2 storage. *J. Nat. Gas Sci. Eng.* **2020**, *79*, 103361. [CrossRef]
168. Carroll, S.; Hao, Y.; Aines, R. Geochemical detection of carbon dioxide in dilute aquifers. *Geochem. Trans.* **2009**, *10*, 4. [CrossRef]
169. Li, D.; Ren, S.; Rui, H. CO_2 Leakage Behaviors in Typical Caprock-Aquifer System during Geological Storage Process. *ACS Omega* **2019**, *4*, 17874–17879. [CrossRef]
170. Vialle, S.; Ajo-Franklin, J.; Carey, J.W. *Geological Carbon Storage: Subsurface Seals and Caprock Integrity*; Geophysical Monograph; Wiley: Hoboken, NJ, USA, 2019; Volume 238.
171. Manceau, J.C.; Hatzignatiou, D.G.; de Lary, L.; Jensen, N.B.; Réveillère, A. Mitigation and remediation technologies and practices in case of undesired migration of CO_2 from a geological storage unit—Current status. *Int. J. Greenh. Gas Control* **2014**, *22*, 272–290. [CrossRef]
172. Wilke, F.D.H.; Vásquez, M.; Wiersberg, T.; Naumann, R.; Erzinger, J. On the interaction of pure and impure supercritical CO_2 with rock forming minerals in saline aquifers: An experimental geochemical approach. *Appl. Geochem.* **2012**, *27*, 1615–1622. [CrossRef]
173. Ahmad, A.A.; MSaaid, I.; Muhammad, M.A.; Husein, N.; Zaidin, M.F.; Mohamad Sabil, K. Physical and chemical effect of impurities in carbon capture, utilisation and storage. *J. Pet. Explor. Prod. Technol.* **2023**, *13*, 1235–1246.
174. Zaidin, M.F. Thermophysical Properties of CO_2 Aqueous Solutions and the Impact of H_2S on CO_2 Storage. 2020. Available online: https://www.ros.hw.ac.uk/handle/10399/4465 (accessed on 19 July 2024).
175. Labus, K.; Suchodolska, K. Predicting the Interactions of H_2S-CO_2 Mixtures with Aquifer Rock, based on Experiments and Geochemical Modeling. *Procedia Earth Planet. Sci.* **2017**, *17*, 288–291. [CrossRef]
176. Clark, D.E.; Oelkers, E.H.; Gunnarsson, I.; Sigfússon, B.; Snæbjörnsdóttir, S.Ó.; Aradottir, E.S.; Gíslason, S.R. CarbFix2: CO_2 and H2S mineralization during 3.5 years of continuous injection into basaltic rocks at more than 250 °C. *Geochim. Cosmochim. Acta* **2020**, *279*, 45–66. [CrossRef]
177. Amin, S.M.; Zaidin, M.F.; Azuddin, F.J.; Razak, A.A.; Mohsin, N.; Pin, Y.W.; Tewari, R.D. Laboratory and Modelling Study on Comparison of Geochemical Reactivity in Carbonate Reservoir Due to CO_2 Injection with/without the Presence of H2S at High Temperature and Pressure. In Proceedings of the Offshore Technology Conference Asia, Kuala Lumpur, Malaysia, 27 February–1 March 2024.
178. Turnbull, J.C.; Keller, E.D.; Norris, M.W.; Wiltshire, R.M. Atmospheric monitoring of carbon capture and storage leakage using radiocarbon. *Int. J. Greenh. Gas Control* **2017**, *56*, 93–101. [CrossRef]
179. Bilardo, U.; Panvini, F. Carbon Sequestration: Key Features and Issues. Available online: http://onepetro.org/OMCONF/proceedings-pdf/OMC07/All-OMC07/1832810/omc-2007-036.pdf (accessed on 21 May 2024).

180. Fang, Z.; Khaksar, A.; Gibbons, K.; Hughes, B. Geomechanical Risk Assessments for CO_2 Sequestration in Depleted Hydrocarbon Sandstone Reservoirs. 2012. Available online: http://onepetro.org/DC/article-pdf/27/03/367/2091406/spe-133994-pa.pdf/1 (accessed on 21 May 2024).
181. Ning, Y.; Tura, A. Wellbore Integrity Impact on Carbon Leakage to Ensure Safe Geological Sequestration. In Proceedings of the SPE Annual Technical Conference and Exhibition, Houston, TX, USA, 3–5 October 2022. [CrossRef]
182. Moghanloo, R.G.; Yan, X.; Law, G.; Roshani, S.; Babb, G.; Herron, W. Challenges Associated with CO_2 Sequestration and Hydrocarbon Recovery. In *Recent Advances in Carbon Capture and Storage*; InTech: London, UK, 2017.
183. Li, D.; Zhang, L.; Ren, B.; Ren, S. Experimental Study of CO_2-Sensitive Chemicals for Enhanced Sealing of Leakage Pathways in CO_2 Geological Storage Process. *Energy Procedia* **2014**, *63*, 4646–4657. [CrossRef]
184. Fatah, A.; Norrman, K.; Al-Yaseri, A. Surface Chemistry and Chemical Structure of Shale Caprocks Exposed to CO_2: Implication for Sealing Integrity. *Energy Fuels* **2024**, *38*, 4390–4400. [CrossRef]
185. Martin, F.D.; Taber, J.J.; Mexico, N. Because of the Minimum Pressure Requirement Carbon Dioxide Flooding. 1992. Available online: http://onepetro.org/JPT/article-pdf/44/04/396/2223032/spe-23564-pa.pdf/1 (accessed on 4 June 2024).
186. Hameli, A.; Dhuhoori, A.; Gomes, P.; Al Hameli, F.; Belhaj, H.; Al Dhuhoori, M. CO_2 Sequestration Overview in Geological Formations: Trapping Mechanisms Matrix Assessment. *Energies* **2022**, *15*, 7805. [CrossRef]
187. Chen, B.; Harp, D.R.; Lin, Y.; Keating, E.H.; Pawar, R.J. Geologic CO_2 sequestration monitoring design: A machine learning and uncertainty quantification based approach. *Appl. Energy* **2018**, *225*, 332–345. [CrossRef]
188. Shi, Z.; Driba, D.L.; Rivera, N.L.; Kariminasab, M.; Beckingham, L.E. A Review of Coupled Geochemical–Geomechanical Impacts in Subsurface CO_2, H_2, and Air Storage Systems. *Energies* **2024**, *17*, 2928. [CrossRef]