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Review

A Review of the Studies on CO$_2$–Brine–Rock Interaction in Geological Storage Process

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Abstract: CO$_2$–brine–rock interaction impacts the behavior and efficiency of CO$_2$ geological storage; a thorough understanding of these impacts is important. A lot of research in the past has considered the nature and impact of CO$_2$–brine–rock interaction and much has been learned. Given that the solubility and rate of mineralization of CO$_2$ in brine under reservoir conditions is slow, free and mobile, CO$_2$ will be contained in the reservoir for a long time until the phase of CO$_2$ evolves. A review of independent research indicates that the phase of CO$_2$ affects the nature of CO$_2$–brine–rock interaction. It is important to understand how different phases of CO$_2$ that can be present in a reservoir affects CO$_2$–brine–rock interaction. However, the impact of the phase of CO$_2$ in a CO$_2$–brine–rock interaction has not been given proper attention. This paper is a systematic review of relevant research on the impact of the phase of CO$_2$ on the behavior and efficiency of CO$_2$ geological storage, extending to long-term changes in CO$_2$, brine, and rock properties; it articulates new knowledge on the effect of the phase of CO$_2$ on CO$_2$–brine–rock behavior in geosequestration sites and highlights areas for further development.

Keywords: phase CO$_2$; CO$_2$ geological storage; CO$_2$–brine–rock interaction; reservoir; net-zero target

1. Introduction

According to the IPCC 2021 AR6, geological CO$_2$ storage is a promising method for achieving the net-zero target by 2050. It is also vital for achieving the net-negative target. However, there are concerns about the changes that occur in the reservoir properties due to CO$_2$–brine–rock interaction and its implication on the behavior of the reservoir and the efficiency of the storage process. CO$_2$–brine–rock interaction has been shown to cause changes that could be constructive or deleterious to the ability of the reservoir to safely store CO$_2$ (Delle and Sarout [1], Xiao et al. [2], Valle et al. [3], Nguyen [4] and Fuchs et al. [5]). We present a review of recent research on these issues. The scope of this review covers the effect of all phases of CO$_2$–brine on the physical, geomechanical, mineralogical, and petrophysical properties of reservoir rocks, and the implications for the behavior of the reservoir and the efficiency of the storage process. Firstly, we examine the different types of reservoirs and their different capacities. Secondly, we discuss the long-term changes to CO$_2$ and brine in deep reservoirs. Thirdly, we present the effect of different phases of CO$_2$–brine on the different properties of rock. We conclude by discussing the trends in geological storage research, highlighting the needs and direction for future studies. This review extends the understanding of CO$_2$–brine–rock interaction and its effect on CO$_2$, brine, and rock properties; it articulates new knowledge on the effect of the phase of CO$_2$ on CO$_2$–brine–rock behavior in geosequestration sites and highlights areas for further development.

Geological CO_2 storage should be given significant attention, especially now that the global primary energy consumption for fossil fuels is predicted to keep increasing until 2050 [6], see Figure 1. This trend will continue and may increase until impactful actions are taken to reverse the trend. Geological CO_2 storage involves capturing anthropogenic CO_2 and storing it in suitable geologic reservoirs. Reservoirs that can be used for geological CO_2 storage include saline reservoirs, depleted oil and gas fields, unmineable coal fields, and the ocean. However, some types of reservoirs are preferred over others; this will be discussed later. Over 200 million tonnes of anthropogenic CO_2 have been successfully injected and stored in geologic reservoirs over several decades around the world; over 40 sites are presently and/or have been safely injected with anthropogenic CO_2 for enhanced oil recovery or geological storage [7]. Examples of such sites include the In-Salah carbon capture and storage (CCS) project, Sleipner CCS project, Snohit CCS project, and the Otway carbon reduction commitment (CO_2CRC) project, amongst others. This shows that geological CO_2 storage is a feasible technology for reducing the amount of CO_2 released into the atmosphere. It can be combined with the net-negative emission technologies that have been explained in [8–10] to achieve greater and faster reduction in the amount of CO_2 released into the atmosphere.
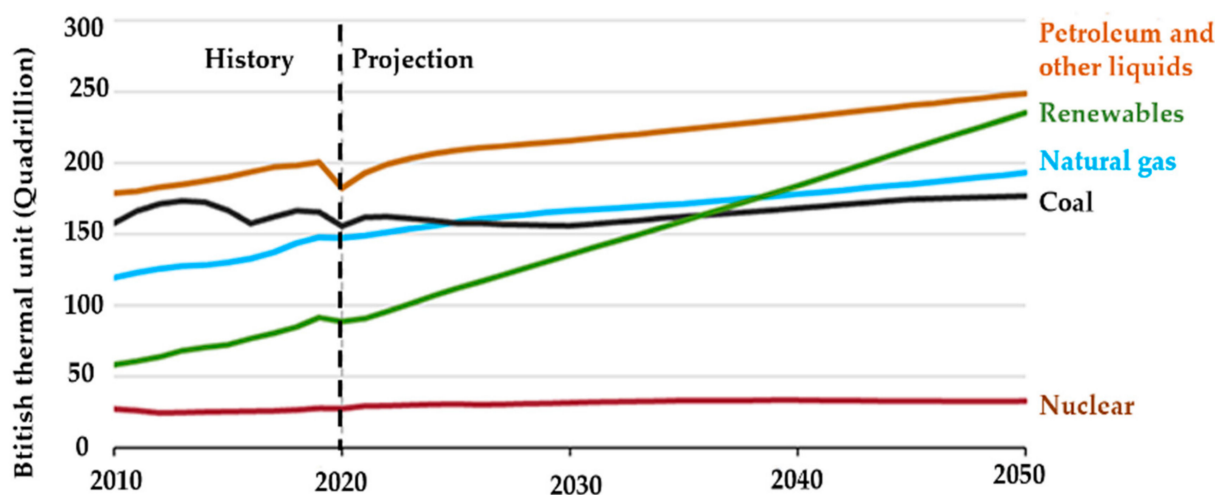

Figure 1. U.S. Energy Information Administration (October 2008), International Energy Outlook 2021 [6]. British thermal unit is the heat of fossil fuel needed to raise the temperature of one pound of water by 1 degree Fahrenheit.

Properties of rocks are very crucial for the performance and efficiency of the storage process. Changes in the properties of the reservoir rocks due to CO_2–brine–rock interaction must be well understood, as some changes can reduce the ability of the reservoir to efficiently and safely store CO_2. Considering the thermodynamics, the phase behavior, the solubility of CO_2 in brine, and the variable pressure-temperature conditions of the reservoir, there will be undissolved CO_2 in the CO_2 storage reservoir alongside the brine for a long time and there will be phase evolution of the undissolved CO_2. Since different Phase CO_2–brine have unique effects on the properties of reservoir rocks, the phase of CO_2 present in the reservoir influences CO_2–brine–rock interaction.

2. Types of Reservoirs and Their Capacities

CO_2 can be stored in saline reservoirs, depleted oil and gas fields, unmineable coal seams, and ocean sinks. This review focuses on saline reservoirs; the capacity of saline reservoirs will be compared with the other geologic reservoirs. However, the storage capacity of other reservoirs will be discussed briefly.

2.1. Saline Reservoirs

Saline reservoirs are deep, porous, and permeable geological formations. The worldwide combined onshore and offshore storage capacity of the saline reservoir is over 1000 gigatonnes of carbon (Gt-C) [11]; however, onshore saline fields are sometimes considered too small and unsuitable to be used for CO_2 geological storage because saline fields are mostly fragmented and are used for agricultural, industrial and groundwater exploitation, etc. purposes. Saline reservoirs offer the greatest storage potential in terms of capacity [12–14]. Presently, most storage sites are in deep saline aquifers; for instance, the In-Salah CCS project and Otway CO_2CRC project are in an onshore deep saline reservoir, and the Sleipner CCS project is in an offshore deep saline reservoir. In the UK, the offshore saline reservoir's theoretical storage is estimated at 78 Gt-C [15].

The drawback of the saline reservoir compared with depleted oil and gas fields is the need to build infrastructure from scratch and the possibility of pressurization especially if the pore pressure due to injection rises too high. Although Kim et al. [16] identify saline reservoirs as the most promising for safe and effective CO_2 storage, Holloway et al. [17] show that the capacity of a saline reservoir must be filtered through the following considerations: (a). Parts of saline reservoirs are sources of potable water for the human population. (b). Reservoirs with the possibility of leakage of the injected CO_2 must be avoided. (c). The target depth for CO_2 storage must be greater than 800 m except where there are large structural or stratigraphic traps above this depth. (d). Over-pressured reservoirs must be avoided. (e). Reservoirs with no viable trapping mechanism and/or seal are considered unsuitable. These considerations are necessary because supercritical CO_2 injected in saline reservoirs takes several hundreds of years to be dissolved in saline reservoirs.

The depth limit of 800 m stated above is because it is assumed that at a depth greater than 800 m, the temperature and pressure of most reservoirs are such that CO_2 will be in the supercritical phase [18], which gives an operational advantage for CO_2 storage. After all, the liquid-like density allows for more volume of CO_2 to be stored per unit pore volume while reducing the buoyancy drive. This depth also allows enough clearance for human activities, the extraction of potable water, and provides enough time for intervention in the event of leakage. Shukla et al. [19] noted that for storage in the saline aquifer to be sustainable, the reservoir must be large and isolated and must have good reservoir properties, i.e., adequate porosity, permeability, depth, thickness, and poroelastic properties. It must have an adjoining caprock with good sealing capacity. Additionally, the mineralogy of the reservoir must be such that the ensuing reactive process do not degrade the reservoir.

2.2. Depleted Oil and Gas Fields

Oil and gas are generated at great depth from organic materials and are normally associated with the displacement of saline fluids [20]. Depleted oil and gas fields are good prospects for CO_2 storage both in offshore and onshore environments, with an estimated worldwide storage capacity of 675-900 Gt-C [11,21]. The operating principle for CO_2 storage in depleted oil and gas reservoirs is the replacement of oil and gas previously contained in pores with CO_2. According to Shukla et al. [19], depleted gas reservoirs are great for CO_2 storage because they have proven capacity to hold gas for long geologic timescales. This storage option has the added benefit of enhanced oil recovery if needed. However, CO_2 injection for storage poses unique challenges compared with injection for enhanced oil recovery, because of the potential to generate low temperature due to CO_2 expansion into the vapor phase during the injection.

Existing facilities and experience in depleted oil and gas fields can be re-used for a CO_2 injection and storage project [17]. This implies that storage in depleted oil and gas fields has a comparative cost advantage over storage in saline reservoirs. However, every CO_2 injection requires a design specific to reservoir conditions, injection rates, and injection stream characteristics [22]. There is a high probability of leakage through existing wells and the depleted oil and gas field has limitations in storage capacity; nonetheless, the capacity

for CO_2 storage in depleted oil and gas fields will increase as more oil and gas fields are depleted [19].

2.3. Mafic and Ultramafic Reservoirs

Mafic and ultramafic rocks are silicate rocks that are rich in magnesium and iron. The presence of reactive magnesium and iron creates an opportunity for CO_2 storage via mineralization. The principle at work in this storage option is the carbonation of Mg, Ca, and Fe to form carbonates that retain CO_2 in stable phases. For instance, Mg-rich olivine is converted to Mg carbonate in the presence of CO_2–brine. This method was proposed about 30 years ago as a long-term and non-toxic method of storing CO_2 in a solid form [14]. It is the most stable long-term storage option. This storage option has great prospects because mafic and ultramafic rocks are abundant, and the reaction is exothermic and will require no heat but will progress at a reasonable rate. Research such as [23] has used deep-sea basalts and [24] has used peridotites and serpentinites to permanently lock up CO_2 as carbonate minerals. There are other studies on the injection of CO_2 in mafic and ultramafic rocks for mineral carbonation [25–29]. These studies show that there is a fast release of Mg just after 2 days and the addition of organic acids increases the rate of mineralization of the mafic silicate minerals. The storage capacity of rocks with potential for mineral carbonation in the Nordic region is put at 62-333 Gt [30]. Factors that affect the storage potential of basaltic rocks include temperature, pressure, PH, water chemistry, porosity, permeability, and CO_2 phase [31]. This method of storing CO_2 still needs a lot of development through pilot and laboratory studies to have a good understanding of the process and how to optimize it. Globally, carbon mineralization in mafic and ultramafic rocks provides a storage potential of 60,000,000 gigatonnes of CO_2 ($GtCO_2$) [14].

2.4. Salt Caverns

Caverns are artificial cavities constructed in the thick salt dome by the solution mining process. Salt caverns are another way of storing CO_2 underground. Storage of CO_2 in salt caverns is due to the great sealing capabilities and excellent mechanical and self-healing properties [32]. In this process, CO_2 is stored in the salt layers of the cavern. Here, there can be re-precipitation of salt. Precipitation of salt can lead to a change in the properties of the rock as the precipitated salt can clog pores and reduce permeability. This will be discussed more later. An extension of the application of this method is its use in purifying fossil fuel during production as the oil extracted from deep reservoirs is made to pass through the salt cavern to reduce the amount of CO_2 and CH_4 emissions. Salt cavern is good for temporary storage. This method is still undergoing development and its biggest challenge is integrity. According to CEDIGAZ, there were 97 salt cavern storage facilities in the world as of 2016.

2.5. Unmineable Coal Seams

Coal becomes unmineable when the calorific value of the coal is not enough to generate good heat, or when a mine has been worked exhaustively at the present level of technology, or when the geologic disposition of the mine is such that it cannot be worked at a profit. These kinds of coal seam provide another opportunity to store CO_2. The mechanism of storage is in the micropores of the coal as free gas or as pore fluid, or by adsorption at the surface of the coal, and methane is released as a byproduct. The former requires that the coal seam has enough micropore spaces that are interconnected, whereas the later requires that the pressure condition of the seam is below the desorption pressure. More research concerning the issues with coal can be found in [33–39]. Yamasaki [35] puts the amount of worldwide CO_2 storage capacity in unmineable coal at 11 Gt-C.

Overall, coal is less preferred for CO_2 storage largely because of the peculiar issues associated with coal and the fact that coal has other competing use. The major issues with CO_2 storage in coal include reduction in strength, low permeability and porosity of coal, and matrix swelling that affects storage capacity of coal especially when the mechanism of storage is adsorption. Consequently, there is a high chance of leakage from unmineable

coal. This has costly economic, environmental and health implications and explains why coal is not a good candidate reservoir for CO_2 storage.

2.6. Ocean Sinks

Ocean storage entails the use of large bodies of water, sediments, and biomass to store CO_2 through their natural processes. Oceans are giant carbon sinks with the capacity to store CO_2 in gigatons and research has shown that this can contribute to meeting the net-zero target [40]. The tendency of CO_2 to dissolve in oceanic waters, photosynthesis by biomass (phytoplanktons), and the capacity of sediments to form carbon dioxide hydrates are the principles that are used in this storage option. As CO_2 dissolves into the oceanic water, the aqueous CO_2 combines with the water to form carbonic acid, the carbonic acid continues to react with the water to precipitate Carbonates. There is an increase in the concentration of Carbonates and hydrogen ions, and a consequent reduction in the pH of the oceanic water, this is known as acidification. Metz et al. [41] showed that acidification of oceanic water leads to the destruction of the marine ecosystem. However, Caldeira et al. [42] reported that dilute carbon dioxide injection at 0.37 GtC/yr would have a negligible effect on ocean pH, this was inferred from measurements of natural pH fluctuations from atmospheric carbon dioxide.

The release of CO_2 into the ocean can be carried out in dilute, solid, or hydrate form. This is usually carried out at about 1000 m depth to ensure efficient mixing and dissolution of CO_2 in water. Oceanic storage of CO_2 is best conducted at great depth to prevent the escape of CO_2 bubbles. CO_2 can also be stored in the deep ocean sediment, where CO_2 is injected below the water directly into ocean sediments, and hydrate is formed. Hydrates forms as an external layer around liquid carbon dioxide droplets or as a solid mass, and this takes place when the dissolved concentration of the aqueous CO_2 is around 30% and at about 400 m below sea level, and also dissolves at a rate of about 0.2 cm/h [43]. Caldeira et al. [42] demonstrated that CO_2 can be injected into oceans as a rising and sinking plume. As the plume mixes with oceanic water, it becomes denser than the seawater and sinks. Sinking and dissolution are continuous by convection and action of the water current. The sinking plume of CO_2 water forms a lake at the bottom of the ocean for long-term sequestration. Caldeira et al. [42] also reported that solid CO_2 dissolves at a rate of about 0.2 cm/h, implying that only a small quantity of carbon dioxide can be completely dissolved before reaching the seafloor. Mineralization occurs in the ocean after dissolution and sinking at the bottom of the ocean. Goldthorpe [44] showed that oceanic CO_2 storage could be viable for up to 500 years but is dependent specific on-site conditions. Factors that affect the rate of dissolution of CO_2 include temperature, pressure, viscosity, concentration and depth of the water as well as solubility, density, viscosity and the concentration of CO_2.

The oceanic storage option is the least developed and the least favorable for CO_2 storage because of the great environmental risk it poses to the marine ecosystem. Metz et al. [41] showed the impacts of oceanic CO_2 storage before and after injection to include the death of biota, reduced reproduction rate, the evolution of biota, change in the chemical and physical composition of the surface water, acidification. The results show that the impact of CO_2 is spatially limited and the organisms that occupy that space will be significantly affected instantly. Proponents of oceanic storage argue that there are strong uncertainties in these researches and that due to the size of the ocean, injected CO_2 will not be able to cause a serious impact on the ecosystems and that species can evolve to adapt to the increased level of CO_2 dissolved in the water. There is no evidence to support the capacity of organisms to evolve and adapt to increased CO_2 levels. Table 1 presents a summary of the capacities of different types of reservoirs.

Table 1. Worldwide CO_2 storage capacities in different reservoirs.

Storage Option	Capacity	Source
Oil and gas fields	675–900 Gt-C	[11,21]
Unmineable coal seams (This has been abandoned)	3–200 Gt-C	[11,35]
Deep saline fields	>1000 Gt-C	[11]
Mafic and ultramafic rocks	60,000,000 Gt-C	[14]
Cavern storage	-	-

3. Long Term Changes in CO_2, Brine, and the Reservoirs

Once CO_2 is injected into a reservoir for storage, it mixes with the fluid in the reservoir, and the properties of CO_2, brine, and the reservoir change over time. The density of CO_2-bearing brine is higher than brine; thus, CO_2-saturated brine sinks to the bottom. This process of density settling creates hydrodynamic processes that are necessary for CO_2–brine mixing and dissolution. The undissolved CO_2 is lighter and rises to the top of the mix by buoyancy. An illustration of the process of geological CO_2 storage starting from the injection stage to the evolution of the phase of stored CO_2, and the storage in pore spaces and strata is shown in Figures 2 and 3.
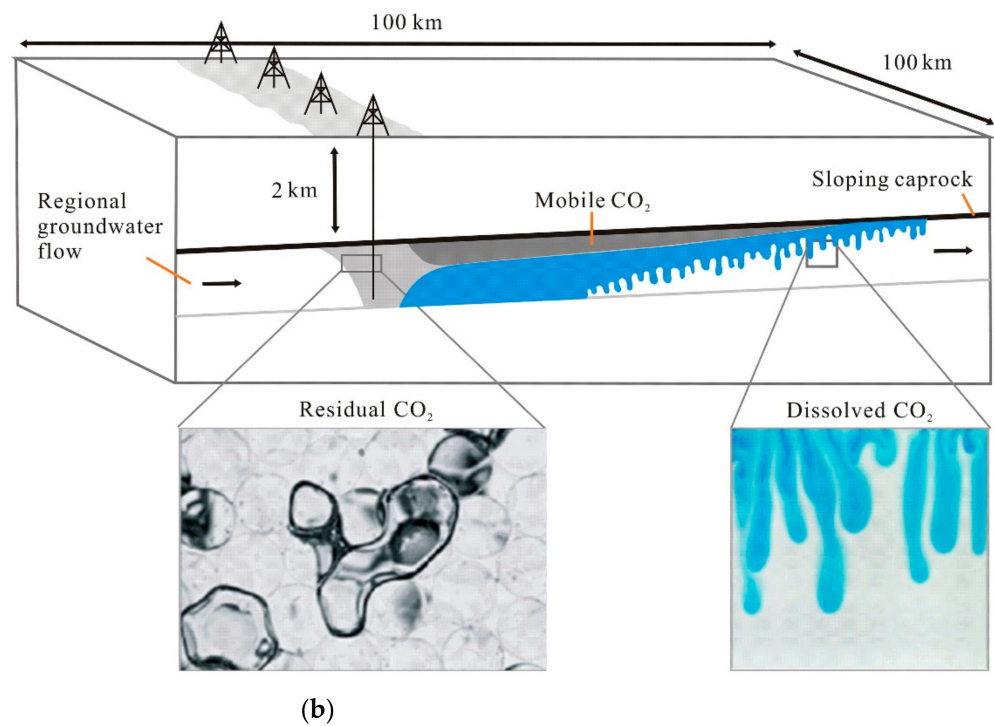

(a)

Figure 2. *Cont.*

(**b**)
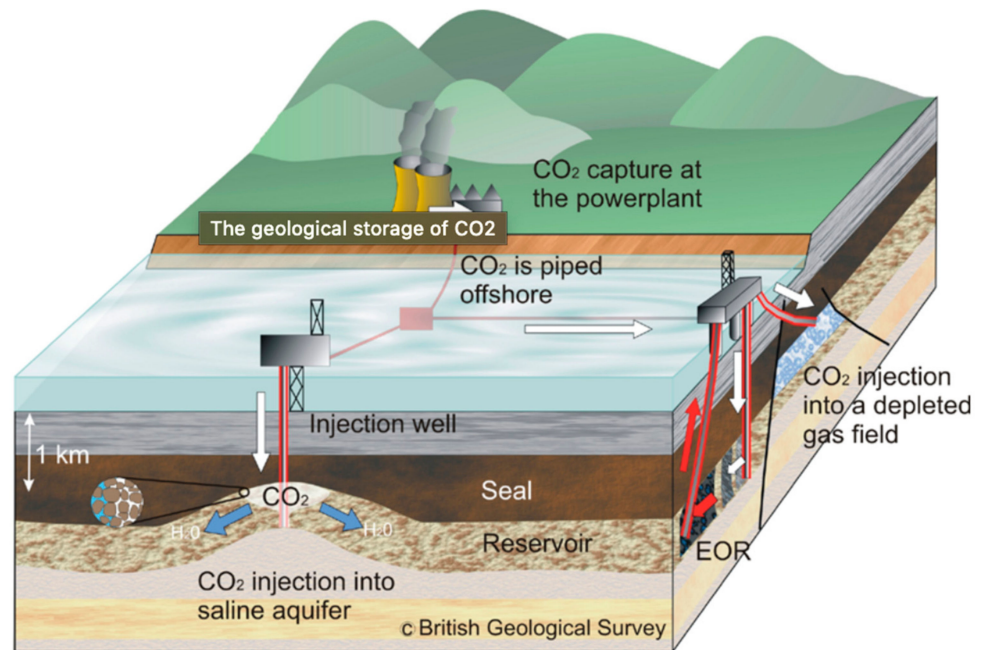
Figure 2. An illustration of the geological CO_2 storage from injection to storage shows the evolution and mobility of the stored CO_2 and eventual trapping. (**a**) schematic of CO_2 injection for storage (reprinted with permission from [45]. © 2022. UKRI), (**b**) schematic of CO_2 trapping mechanism (reprinted with permission from [46]. ©2016. JRMGE). A similar illustration of these processes can be found in [47,48] for comparison.

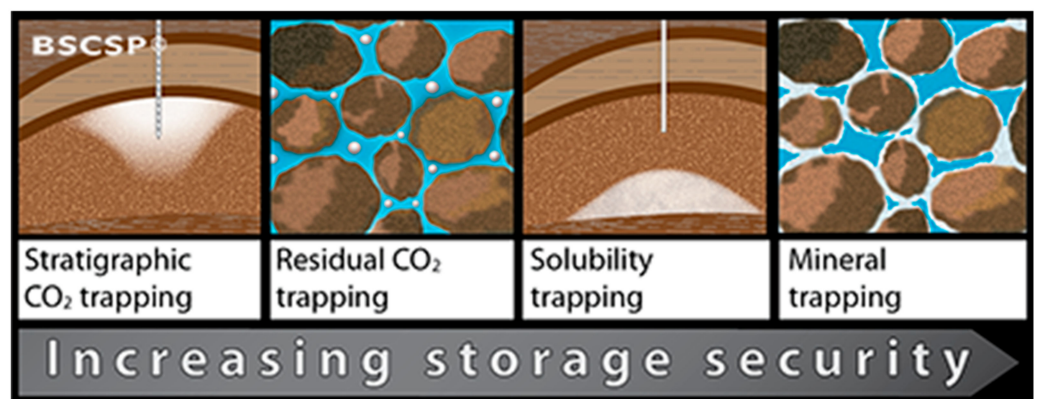**Figure 3.** An illustration of different CO_2 trapping mechanisms. Reprinted with permission from [49]. ©2022. Montana State University.

Table 2 presents a summary of recent research on different thematic issues concerning long-term changes in CO_2–brine and the reservoir. The research covered is systematically collated based on the issue investigated and its recentness. It is not exhaustive.

Table 2. Summary of research on long-term changes to CO_2–brine and reservoirs.

a. Density, Solubility, and Viscosity of CO_2		
Authors	CO_2-brine state	Findings
Jeon and Lee [50]	gCO_2, $ScCO_2$ and brine	Studied the effect of viscosity ratio and interfacial tension using unsteady-state relative permeability experiments. Viscosity ratio is the ratio of the viscosity of the solution to the solvent, whereas interfacial tension is the force of attraction between molecules at the interface of two fluids. A dual high-pressure separator was used to measure the fluid saturation. They found a high residual brine saturation of the two-phase CO_2–brine system and showed that relative permeability depends on the viscosity ratio and interfacial tension of CO_2–brine.
Chabab et al. [51]	gCO_2 and brine	Extended the Soriede and Whitson model to develop a model that predicts the water content and solubilities of CO_2 and other gases in different types of brine over a range of temperature and pressure. This developed model has been successful in predicting bubble point pressure and gas emissions by comparing its result with data from geothermal power plants.
Li et al. [52]	gCO_2 and brine	Found that an increase in salinity reduces the solubility of CO_2 in brine in nanopores
Lara Cruz et al. [53]	Aqueous CO_2 and mixture of $CaCl_2$ and $NaCl$	Showed the solubility of CO_2 in $NaCl$ and $CaCl_2$ brines at pressures up to 40 Mpa and a temperature range of 333.15–453.15 K. Their results showed that the solubility of CO_2 decreases as the aqueous phase salinity increases.
Enick and Klara [54], Song et al. [55]	gCO_2 and and Water or brine	Showed that the solubility of CO_2 varies with temperature, pressure, and composition of the brine, the correlations show a wide scatter in each case but there was a decrease in solubility of CO_2 in brine at a temperature range of 298 to 523 K and pressure range of 3.0 to 85.0 MPa.
Jamshidi et al. [56]	gCO_2 and brine, and gCO_2 and heavy oil	Showed that the solubility of CO_2 in heavy oil increased as pressure increased and as temperature decreased.
Chebab et al. [57]	-	The static analytic method was used to measure the solubility of CO_2 and model phase equilibria. The Peng–Robinson Cubic Plus Association (PR-CPA) model which uses cubic equations of state (EOS) for determining the properties of fluid was extended to electrolyte-CPA and the Soriede and Whitson model for determining the properties of petroleum fraction was improved. Duan model in software was tested. The improved models were tested with a wide range of temperature, pressure, and molality. The new models were validated against data in the literature and performed well.
Hajiw et al. [58]	gCO_2 and pure water	Evaluated the impact of impurities from flue gases on the solubility of CO_2 in water by vapor-liquid equilibria (VLE) calculations using a geochemical model and thermodynamic models such as the Group Contribution-Peng–Robinson-Cubic Plus Association (GC-PR-CPA) and the Enhanced Predictive Peng–Robinson (E-PPR78) equation of state models. These impurities were noted to increase the density, viscosity and alter the behavior of CO_2. The GC-PR-CPA and geochemical model give results agreeable with literature data, but, this was dependent on the availability and quality of data
Ali Ahmadi and Ahmadi [59]	CO_2 and brine	Used the least square support vector machine (LS-SVM) to predict the solubility of CO_2 in brine and showed that solubility of CO_2 increases with decreasing temperature. The result from the LS-SVM method proved to be more reliable robust and compatible than other conventional methods such as Whiteson and modified Whitson methods under certain conditions.
Jacob and Saylor [60], Ratnakar et al. [61]	gCO_2 and $NaCl$, $CaCl_2$, KCl and a mixture of all the brine	Showed that the ionic composition of brine affects the solubility of CO_2. Solubility was shown to decrease with an increase in salt content in single component brines, whereas solubility in multi-component brines was shown to depend on the salt present.

Table 2. *Cont.*

Mohammadian et al. [62]	gCO_2 and NaCl brine	Presented solubility data of CO_2 in brine for a salinity range of 0–15,000 ppm, temperature range of 60–100 °C, and pressure up to 25 MPa. Measurement was carried out using the potentiometric titration method. An increase in pressure caused increased solubility of CO_2 in distilled water and brine and vice versa for an increase in temperature. An increase in salinity reduces solubility. The reduction in the solubility is by about 13% as the salinity increases by 1.5% from an initial state of 0. The solubility obtained was consistent with those obtained from other methods.
Lamy-Chappuis [63]	gCO_2 and brine	Provided estimates of the changes in density, and viscosity of CO_2 at depths >800 m. Density and viscosity of brine are controlled by temperature, pressure, and salinity of the brine, and affect the convection current and rate of dissolution. CO_2 density was found to be about 20% higher at injection pressure than at hydrostatic pressure below 800 m. 1 M and 5 M NaCl-brine were used, the addition of salt to water was seen to result in a 10% increase in density and an 80% increase in viscosity.
Yan et al. [64]	gCO_2 and NH_4Cl or $NaHPO_4$ brine	Presented solubility data of CO_2 in brine and water under different temperatures, pressure, and salinity. The result showed that the dissolution of CO_2 increases the brine density if the mass density of CO_2 in brine is higher than the density under the same conditions. At high salinity and temperature, the dissolution of CO_2 decreases the brine density
b.	**Density and Viscosity of Brine**	
Tatar et al. [65]	-	Used radial basis function neural networks and genetic algorithm to predict the density of brine
Mao and Duan [66]	-	Developed a temperature, pressure, and salt content (P, V, T, x) model for calculating the density and viscosity of brine under varying temperature, pressure, and salinity conditions. This model compares well with previous experimental data with an average deviation of only 0.020% to 0.066% in density
c.	**Solubility, Density, and Viscosity of CO_2-Saturated Brine**	
Li et al. [52].	gCO_2–brine	Investigated the impact of pH on solubility of CO_2 in brine and found that the solubility of CO_2 in brine reduces as the pH increases
Teng et al. [67].	CO_2 saturated brine and only brine	Showed that an increase in viscosity contrast between CO_2 and brine hinders density-driven convection and slows down the rate of solubility
Mahmoodpour et al. [68]	gCO_2 and NaCl or mixture of NaCL and $CaCl_2$	Studied the effect of brine composition on the onset of convection. They showed the onset of convection for a brine solution containing NaCl occurs earlier and with a higher wavenumber, whereas a mixture of NaCl and $CaCl_2$ results in a late-onset of convection and a higher CO_2 diffusion coefficient. This implies that the onset of instabilities and fingering in a multi-ion brine is delayed compared with a single ion brine
Islam et al. [69]	gCO_2 and brine	Showed that the convection current is a hydrodynamic process that promotes the mixing and dissolution of CO_2 in brine
Liu et al. [70]; Mosavat and Torabi [71].	CO_2 and NaCl, $CaCl_2$, KCl and a mixture of all the brine	Shows that an increase in pressure leads to an increase in the solubility of CO_2, whereas an increase in temperature leads to a decrease in solubility of CO_2 in brine
Duan et al. [72], Mao et al. [73]; Ahmad et al. [74].	gCO_2 and water or CO_2-H_2O-NaCl	Reported an increase in density and a decrease in the buoyancy of CO_2 when it dissolves in brine

Table 2. *Cont.*

d. Relative Permeability, Capillary Pressure, and Fingering		
Jeong et al. [75]	gCO_2 and brine	Found that the endpoint permeability of CO_2 increases as the residual brine saturation decreases and as the flow rate increases
Abdoulghafour et al. [76]	Liquid CO_2–brine	Reported that low capillary pressure promotes high residual CO_2 saturation and improved capillary trapping
Basirat et al. [77]	$scCO_2$ and gCO_2 with N_2 and CH_4 impurities.	Posited that the wetting condition of the reservoir affects the relative permeability, CO_2 breakthrough, and saturation. The wetting condition is the fluid that surrounds the grains and fills the pores, saline rocks are water wet. Strongly water-wet rock was seen to significantly reduce the relative permeability of CO_2 This provides a suitable condition for dissolution trapping due to an increase in the interfacial angle between CO_2 and brine. Water wet conditions also enhanced the capillary effect, which is helpful for residual trapping. A decrease in water-wet conditions increased the saturation of the wetting phase and interfacial area. The results showed no clear relationship between breakthrough, saturation, and wetting condition
Sidiq et al. [78].	gCO_2	Showed that the capillarity end effect in measuring relative permeability can be minimized by using longer cores
Jeong et al. [79]	gCO_2 and brine	Reported that relative permeability is a function of viscous force and injection rates
Ajibola et al. [80].	gCO_2 and water	Showed that difference in density and vertical permeability had great control on fingering
Shukla and De Wit [81]	-	Showed that fingering can also be caused by a change in mobility due to precipitation reaction decreasing the permeability of the medium
Al-Menhali et al. [82]; Jung and Hu [83].	Liquid and supercritical CO_2	Showed the impact of reservoir conditions such as pressure, temperature, and salinity on the capillary strength and interfacial tension. At a given salinity, increasing the temperature and the transition from liquid to supercritical CO_2, there was a small weakening of the capillary strength and a small increase in interfacial tension. With an increase in pressure, and pressure range within the gaseous, low-density supercritical, and high-density supercritical phase, the interfacial tension between the fluids decreased. With an increase in temperature and the temperature range within the liquid or supercritical phase, the interfacial tension increases. With an increase in salinity, and at constant temperature and pressure, the interfacial tension increased
Reynolds and Krevor [84]	gCO_2, brine and N_2-water	Showed that reservoir conditions have little impact on relative permeability and residual trapping. They further showed that relative permeability is sensitive to capillary heterogeneity in the rock. With capillary heterogeneity in the rock, capillary-driven flow redistributed fluid. The effective relative permeability curves were seen to be sensitive to pressure, temperature and brine salinity, and flow rate. At a constant flow rate, the relative permeability minimized the capillary end effects
e. Multiphase Flow of CO_2–brine		
Krevor et al. [85]	gCO_2 and NaCl	Showed that reservoir heterogeneity has little impact on the multiphase flow of CO_2–brine in the reservoir
Saeedi et al. [86]	-	Found that flooding cycles affect the multiphase flow characteristics in the CO_2–brine system. The flooding cycle is the alternating CO_2–brine injection or periodic CO_2 injection. The effect of cyclic flooding on saturation is minimal but strongly influences differential pressures across the medium. These effects are due to capillary hysteresis, the reaction between the solute and host rock, stress, and changes to the reservoir due to CO_2 or alternating CO_2–brine injection
Kuo et al. [87]	gCO_2 and brine	Displayed the effect of viscous, capillary, and gravity forces on displacement efficiency. They showed that when injection rates are large enough, the flow is dominated by viscous forces, but when the injection rate is low, the flow is dominated by capillary forces. Gravity forces are negligible

Table 2. *Cont.*

	f.	**CO_2 Injection and Long Term Evolution**
Vilarrasa et al. [88]	gCO_2	Observed that CO_2 reaches the bottom of injection wells at a colder temperature. This cooling and overpressure tend to enhance injectivity
Pruess and Nordbotten [89]	gCO_2	Reported that the process of long-term CO_2 plume advancement differs from that of forced immiscible displacement. Instead of the fluid being pushed forward, the fluid collapses ahead of the plume tip. This is because the vertical pressure gradient in the plume is smaller than the hydrostatic pressure
Xu et al. [90]; Whittaker et al. [91]	gCO_2	Found a significant drop in the pH of brine over time; observed that CO_2 plume expands gradually due to capillary forces and that gas saturation gradually decreases due to its dissolution and the precipitation of Carbonates. The gas-phase was predicted to disappear after 500 years

From the summary in Table 2, it is seen that the transport and reservoir properties in a geosequestration site are intricately dependent on each other. Any change in a property will affect a chain of other properties. For instance, Jeong et al. [75] showed that permeability depends on viscosity ratio and interfacial tension. Other factors that have been shown to affect permeability are capillary heterogeneity, fingering, and miscibility. This shows that geosequestration sites are sites of complex hydro-chemo-mechanical processes that require careful study. It is also shown that properties of CO_2–brine such as density, viscosity, and solubility are massively affected by temperature, pressure, and salinity of the brine [54–56,62]. The pressure and temperature conditions of the reservoir are dynamic, and the salinity of brine changes depending on the amount of dilution at any given time. This means that the flow properties of CO_2–brine in the saline reservoir will change over time. It is very important to be able to evaluate the density and viscosity of CO_2–brine under the changing reservoir conditions. Models proposed by Ali and Ahmadi [59], Tatar et al. [65], Mao and Duan [66], and Mao et al. [73] have been successful at predicting the density and viscosity of CO_2–brine under different temperatures, pressure, and salinity, with each model having varying levels of accuracy.

A review of the literature shows that CO_2–brine–rock studies mainly assume static reservoir and flow properties. However, Rochelle et al. [43] showed that CO_2 can exist in different phases at different depths in the reservoir. This is illustrated in Figure 4, where CO_2 exists in solid hydrate form under the sea bed, and as gaseous or liquid CO_2 at a greater depth where temperature and pressure are higher. It is our opinion that research that considers CO_2–brine–rock interaction as a dynamic process is needed to provide a better understanding of the process.

Ilgen et al. [92] and Rutqvist [93] showed that chemical and mechanical changes in the properties of reservoir rocks are coupled. Therefore, a change in the chemical composition of the rocks by dissolution, precipitation, or pore stress corrosion will lead to a change in the bulk modulus, strength, and elastic modulus of the rocks. This has been validated by [Xiao et al. [2], Valle et al. [3], Nguyen [4], Fuchs et al. [5], and Peter et al. [94]. The reservoir conditions affect the CO_2–brine flow; for instance, Jeong et al. [75] reported that the permeability of CO_2 increases as the residual brine saturation decreases, whereas Abdoulghafour et al. [76] found that low capillary pressure promotes high residual CO_2 saturation. On the other hand, the flow of CO_2–brine affects the rock by the dissolution of minerals, precipitation of new minerals, and weakening. This is the reason constant monitoring and prediction of CO_2–brine–rock interaction in any geosequestration site is necessary. It will be counter-productive if the effect of CO_2–brine on rock compromises the integrity of the reservoir and causes leakage. It is important to understand the nature of CO_2–brine–rock at any time to properly predict the effect of CO_2–brine on the rock.

There will be numerous cycles of injection of CO_2 into a reservoir as injection of CO_2 is likely to go on for a long time. Sometimes, the injection of CO_2 into a reservoir can be seasonal depending on the supply of CO_2 and the need for injection. Saeedi et al. [86] showed

that the flooding cycle affects the performance of the reservoir, whereas the effect of cyclic flooding on saturation was seen to be minimal, differential pressures across the medium were strongly affected. This means that reservoirs managers will need more proactive actions to manage the differential pressure as the number of cycles of injection increases. Such actions can include increasing the injection so that the flow is dominated by viscous forces to create a better displacement efficiency [87], increasing water-wetness to increase the interfacial angle between CO_2 and brine, and improving dissolution trapping [77].
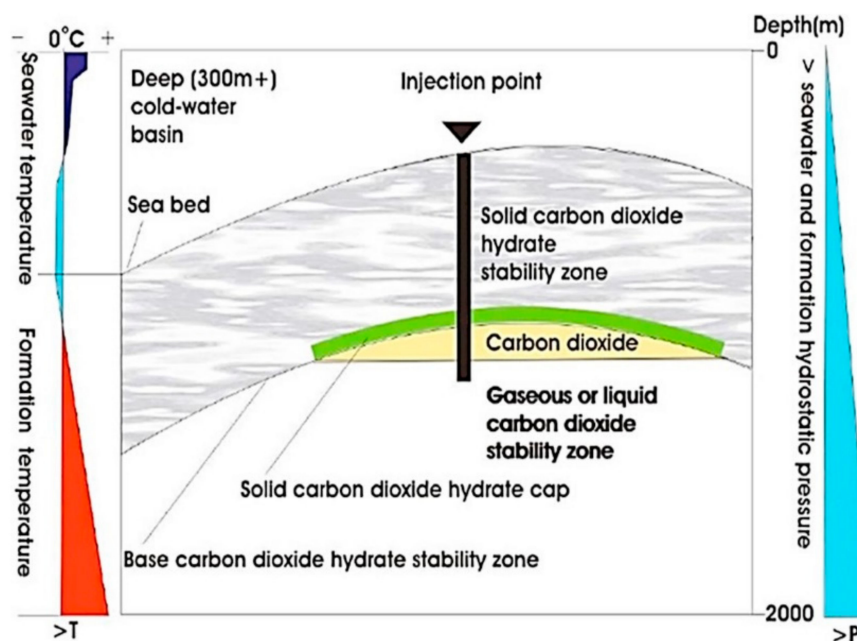

Figure 4. Schematic of different phases of CO_2 underneath the seabed. Reprinted with permission from [43]. © 2009. The geological society of London.

Hydrodynamic instability such as fingering is favorable for CO_2–brine mixing, and Mahmoodpour et al. [68] showed that single ion brine allows for the quicker onset of fingering compared with multi-ion brine. Similarly, Jacob and Saylor [60] showed that the solubility of CO_2 in brine decreased with an increase in salt content for single-component brines, whereas the solubility in multi-component brines was seen to depend on the nature of the salts present but not the concentration of the salts. This means that the brine used in CO_2 flooding experiments must be representative of the brine in the reservoir.

4. Effect of Different Phases of CO_2–Brine on the Different Properties of Rocks

CO_2–brine rock interaction affects the chemical composition, petrophysical and geomechanical properties of the rock. A summary of research on the effects of CO_2–brine on different properties of rock is shown in Table 3.

Caprock is rocks that act as seals and prevent the upward and outward migration of CO_2. They are different from reservoir rocks in that they have finer grains and pore sizes and have much less pore connectivity. Mineralogically, they have higher clay and organic matter content compared with the reservoir rocks. Because of the difference in the petrophysical properties and mineralogy of the caprock, the impact of CO_2 on the properties of the caprock is also different. Examples of caprock include shale, clay, and mudrocks. Recent and relevant research on the effect of CO_2 on different caprock is summarized in Table 4.

Table 3. Summary of research on the effects of CO_2–brine on different properties of reservoir rocks.

Author	State of CO_2	Pore Fluid	Rock Type	Contributions
a. Effect of CO_2–brine on the chemical composition of reservoir rocks				
Peter et al. [94]	$scCO_2$, gCO_2	NaCl brine	Sandstone	These researches show that CO_2–brine–rock processes affect the geochemical and geomechanical properties of the rocks through dissolution, precipitation, or stress corrosion. In sandstone, porosity increased significantly and there was a reduction in fracture toughness by clay-cement weakening. There was a reduction in bulk modulus and strength and an increase in the rate of deformation, there was a loss of clays. In Carbonates, there was dissoution of calcite. Precipitation of clays was also reported. In shales, porosity decreased due to the precipitation of minerals and there was a reduced risk of induced fractures
Xiao et al. [2]	$CO_{2\,(aq)}$	Samples of limestone and shale from Farnsworth unit CO_2-EOR and GCS demonstration site	Limestone	
Valle et al. [3]	$scCO_2$	-	Carbonate rock	
Xiao et al. [2], Valle et al. [3], Nguyen [4], Fuchs et al. [5]	$scCO_2$	For 5, a Solution of NaCl, $CaCl_2$, KCl, KBr, LiCl, $SrCl_2$, and Borax	Siliciclastic rock	
Pimienta et al. [95]	$scCO_2$	-	Carbonate rock	Found that dissolution of minerals in CO_2–brine increased with residence time
Davila et al. [96]	$scCO_2$	A synthetic mixture of different salts referred to as IBDP-1 and IBDP-2	Sandstone	Reported a fast consumption of silicates that indicates the immediate influence of geochemical alteration on the transmissivity and structure of the rock, they observed that the alteration of the core occurred mostly along the inlet.
b. Effect of CO_2–brine on the petro-physical properties of reservoir rocks				
Han et al. [97]	-	Decane and distilled H_2O	Carbonate rocks	Concluded that CO_2 flooding in Carbonate reservoirs can significantly alter pore network, causing an increase in non-connected pores and a reduction in permeability
Lamy-Chappuis et al. [98]	$scCO_2$	NaCl brine	Calcite-rich sandstone	Reported that a 10% increase in porosity resulted in a 10% decrease in sonic velocity in calcite-rich Cayton bay sandstone saturated with gaseous CO_2–brine
Garcia Rios et al. [99]	$scCO_2$	Solution of $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, NaCl, KCl, Na_2SO_4, and NaBr with and without sulfate	Fractured Limestone	Opined that CO_2–brine reaction occurs mostly in the fracture which serves as flow paths and they observed that fracture permeability increased depending on the dissolution pattern
Grombacher et al. [	$CO_{2(aq)}$	H_2O	Carbonate rocks	Showed change in microstructure due to change in the pore space and dissolution in grain coating cement and formation of cracks around larger grains, these resulted in a reduction in acoustic velocity in Carbonate rocks exposed to CO_2-rich brine
Vialle and Vanorio [101]	$CO_{2(aq)}$	H_2O	Carbonate rock	Observed the damping of S and P-wave velocities due to the effect of reactive CO_2–brine, and concluded that the reduction in velocities was connected to an increase in porosity and permeability of the rock and deformation of micro-fabric
Lei and Xue [102]	gCO_2, lCO_2, $scCO_2$	Distilled H_2O	Sandstones	Reported that P-velocity and rock strength reduced more in sandstone saturated with supercritical CO_2 in comparison to those saturated with gaseous and liquid CO_2

Table 3. *Cont.*

c. Effect of CO_2–brine on the geomechanical properties of reservoir rocks				
Ilgen et al. [92], Rutqvist [93]	-	-	Sandstone	An increase in pore pressure and decrease in temperature due to CO_2–brine led to an increase in stress, and the new stress regime triggered changes in shear, bulk, and elastic moduli, and a reduction in strength, scratch toughness, hardness, permeability, and porosity. There was an enlargement of macropores, increase in porosity, and dissolution of smaller particles. Removal of the mineral mass led to microcracking and compaction that subsequently affected the properties of the rock. Dissolution of intergranular cement and mineral precipitation led to a coupled chemical-mechanical response
Espinoza et al. [103]	Natural CO_2 field	Natural rock as sampled, no synthetic brine	Sandstone	Studied the effect of CO_2–brine on the strength of rocks and reported a reduction in the strength
Pimienta et al. [95]	$scCO_2$	Sodium Iodide (NaI) solution	Calcite-rich rocks	
Delle and Sarout [104]	$scCO_2$	H_2O and dry	Berea sandstone	
Zheng et al. [105]	$CO_{2\,(aq)}$	NaCl brine	Sandstone	
Rinehart et al. [106]	$scCO_2$	Solution of $Ca(NO_3)\cdot2.4H_2O$, $NaNO_3$, $MgCO_3$, and deionized H_2O	Sandstone	Showed that degradation in the elastic moduli, strength, and porosity of the rocks depends on the mineral composition of the rocks
Marbler et al. [107]	$scCO_2$	Formation of H_2O of the North German Basin	Sandstone	
Hangx et al. [108]	$scCO_2$	Solution of NaCl, Mg_2Cl, KCl, $CaCl_2$, $CaCO_3$, and distilled H_2O	Sandstone	
Peter et al. [109]	$scCO_2$ and gCO_2	NaCl brine	Sandstone	They agreed that the effect of CO_2–brine on the bulk modulus and rock deformation is affected by the pore fluid, mineralogy, phase of CO_2, and effective pressure. $scCO_2$ induced a greater change in bulk modulus and strength compared with the gaseous CO_2. Carbonate rocks had a greater change in bulk modulus, strength, and porosity compared with siliciclastic rocks
Hangx et al. [110]	Natural CO_2 field	Natural rock as sampled, with no synthetic brine	Sandstone	
Hangx et al. [111]	$scCO_2$	Solution of NaCl, Mg_2Cl, KCl, $CaCl_2$, $CaCO_3$, and distilled H_2O	Sandstone	
Liteanu et al. [112]	$scCO_2$	Boiled distilled H_2O	Calcite-rich rock	
Grgic [113]	$scCO_2$ and gCO_2	Solution of deionized H_2O and limestone powder	Carbonate rocks	
Han et al. [97]	-	Decane and distilled H_2O	Carbonate rock	Showed that injecting CO_2 into brine-rock system-induced chemo-mechanical processes that reduce the strength of the rock and the induced precipitation led to the closing of pores and micro-fracture, whereas dissolution and pore fluid pressure expands the pores
Delle and Sarout [1]	$scCO_2$	H_2O and Dry	Berea sandstone	
Rutqvist [93]	-	-	Sandstone	
Vanorio et al. [114].	$scCO_2$, $CO_{2\,(aq)}$	H_2O and Brine	Sandstone	

Table 3. *Cont.*

Zhang et al. [115]	scCO$_2$	H$_2$O	Sandstone	These researchers reported that CO$_2$–brine reaction led to a reduction in the strength, bulk, elastic modulus, and permeability of rocks. There was a difference in the number of changes in these properties and these differences are due to differences in the mineral composition of the rocks, phase of CO$_2$, and the Physico-chemical conditions
Zhang et al. [116]	CO$_{2\,(aq)}$	N$_2$ or C$_{1–10}$	Sandstone	
Lamy-Chappuis et al. [98]	scCO$_2$	NaCl	Calcite-rich sandstone	
Grombacher et al. [	CO$_{2\,(aq)}$	H$_2$O	Carbonate rocks	
Bemer and Lombard [117]	-	-	Carbonate rocks	
d.	**Effect of CO$_2$–brine on the transport properties of reservoir rocks**			
Sun and Jessen [118]	-	-	Sandstone	Permeability and porosity of sandstones increased due to brine/CO$_2$
Munoz-Ibanez et al. [119]	LCO$_2$	NaCl brine	Synthetic Sandstone	There was enhanced trapping of CO$_2$ in poorly connected fractured reservoirs.
Wang et al. [120]	-	Multi-ion brine containing SO$_4$, Cl, Na, K, Mg, Ca,	Limestone	Flow and transport properties in rocks with carbonic acid differ from those without carbonic acid. Permeability is seen to increase in the former. This is due to changes in pore body and throat sizes. The viscosity of the brine increases due to dissolution and precipitation.
Jeon and Lee [50]	ScCO$_2$	NaCl, deionized H$_2$O, and AOS	Sandstone	They found a high residual brine saturation of the two-phase CO$_2$–brine system and showed that relative permeability depends on the viscosity ratio and interfacial tension of CO$_2$–brine.
Teng et al. [67]	-	MnCl$_2$ in deionized H$_2$O and D$_2$O in deionized H$_2$O	Porous media	Showed that an increase in viscosity contrast between CO$_2$ and brine hinders density-driven convection and slows down the rate of solubility

Table 4. Summary of research on the effects of CO$_2$–brine on different properties of caprock.

Author	State of CO$_2$	Pore Fluid	Rock Type	Contributions
Xiao et al. [2]	CO$_{2\,(aq)}$	Sample from a CO$_2$-EOR and GCS demonstration site	Shale	CO$_2$–brine–rock processes affect the geochemical and geomechanical properties of the rocks through dissolution, precipitation, or stress corrosion. Precipitation of clays was also reported. In shales, porosity decreased due to the precipitation of minerals and there was a reduced risk of induced fractures
Olabode and Radonjic [121]	CO$_{2\,(aq)}$	-	Shale	The geochemical reactivity of acidic fluid contained in an interconnected pore network of shale triggers a slow reactive process that alters the properties of the rock. They linked the changes in the properties to changes in pore surface area and pore distribution. Induced mineral dissolution or precipitation led to the closing of pores and micro-fracture networks.
Alemu et al. [122]	scCO$_2$	NaCl	Clay-rich and Carbonate-rich shale	Observed higher dissolution of metals into CO$_2$–brine compared with the brine. More metals are dissolved in the Carbonate rich shale

Table 4. *Cont.*

Author	State of CO_2	Pore Fluid	Rock Type	Contributions
Ilgen et al. [92], Rutqvist [93])	-	-	Mudrock	An increase in pore pressure and a decrease in temperature due to CO_2–brine led to an increase in stress, and the new stress regime triggered changes in shear, bulk, and elastic moduli, reduction in strength, scratch toughness, and hardness as well as permeability and porosity.
Espinoza et al. [103]	Natural CO_2 field	Natural rock sample, with no synthetic brine	Shale	CO_2–brine caused a reduction in the strength of rocks
Makhnenko et al. [123]	LCO_2, $scCO_2$	-	Shale	Reported that CO_2–brine reaction led to a reduction in the strength, bulk, elastic modulus, and permeability of rocks
Davila et al. [124]	$scCO_2$	NaCl with sulfate-rich H_2O, calcite, and gypsum	Marl	Observing that the composition of the brine affects the fracture permeability of fractured caprock, they reported a dissolution of calcite and precipitation of gypsum forming a framework.
Jeon and Lee [50]	$ScCO_2$	NaCl, deionized H_2O, and AOS	Mudstone	Found a high residual brine saturation of the two-phase CO_2–brine system and showed that relative permeability depends on the viscosity ratio and interfacial tension of CO_2–brine.

From Tables 3 and 4, it can be seen that different types of rocks have been used for core flooding experiments. The rocks range from sandstone, mudrocks, claystone, shale to Carbonates. This is because each of these rocks has been used in CO_2 geological storage. The fine-grained and less permeable rocks such as shale, claystone, and mudrocks serve as stratigraphic traps, whereas the permeable sandstones and pervious Carbonates serve as the reservoirs in CO_2 geological storage. The effect of CO_2–brine on caprock is different from the effect on reservoir rocks because of the geological difference in their origin and difference in chemical composition and physical properties. There can be layers of claystone, mudrocks, or shale within a thick layer of sandstone or Carbonate rocks, and this makes the study of the CO_2–brine response of the fine-grained and less permeable rocks necessary. There is evidence to suggest that sandstones are better reservoirs for CO_2 geological storage compared with Carbonate rocks; for example, Hangx et al. [108] and Lamy-Chappuis et al. [98] showed that Carbonate rocks have a greater change in bulk modulus, strength, and porosity compared with siliciclastic rocks; they argued rocks that are rich in Quartz show minor changes due to the strong grain to grain contact, whereas calcites undergo significant dissolution and microstructural changes. Similarly, Alemu et al. [122] showed that carbonate-rich shale is more reactive compared with clay-rick shales while observing the dissolution of plagioclase, illite, and chlorites, the precipitation of Carbonates, and the formation of Smectite in Carbonate-rich rocks flooded with CO_2–brine. In their experiment, the clay-rich rocks did not show significant changes, but Analcime was deposited on the clay-rich shale that was flooded with CO_2–brine. Furthermore, Han et al. [97] confirmed that the capability of flow and storage in Carbonate rocks are significantly altered by chemical and physical reactions with CO_2–brine. Their experiment showed the disintegration of grains by dissolution and precipitation of minerals particles in contact with the CO_2–brine stream. These call for caution when Carbonates and calcite-bearing rocks are to be used for CO_2 geological storage.

Primacy triggers of changes in the properties of rocks are temperature, pressure, and stress [92,93], Other triggers include dissolution, precipitation and pores stress corrosion. A change in one property of the rock leads to change in other properties, such as the coupled nature of changes that can occur in a geosequestration site. For instance, Fuchs et al. [5]

showed that an increase in the porosity of sandstone led to a reduction in fracture toughness, Xiao et al. [2] showed that decreased porosity due to precipitation led to a reduced risk of induced fracture, this is thought to be the case when a more stable mineral is precipitated. Additionally, Lamy-Chappuis et al. [125] showed that a 10% increase in porosity led to a corresponding change in the sonic velocity, the sonic velocity is indicative of the strength of the rock. Vialle and Vanorio [126] observed that increase in porosity and permeability of rocks flooded with CO_2–brine was matched with a decrease in P and S wave velocity. This knowledge implies that for any geosequestration site, there can be an index property that should be constantly monitored, from which the changes in other properties of the rocks can be evaluated. However, the index property is accurately measured and the relationship between the index property and the other properties that will be evaluated must be well understood and interpreted.

All researchers reported a decrease in strength, bulk modulus, and elastic modulus, but an increase in porosity and permeability of the rocks due to CO_2–brine activity. However, researchers such as Peter et al. [94] and Xiao et al. [2] reported a decrease in porosity due to CO_2–brine activity, they explained that the CO_2–brine–rock reaction led to precipitation of minerals that clogged the pores and thus reduced the porosity. Han et al. [97], Olabode and Radonjic [121], and Delle and Sarout [1] also reported that induced precipitation leads to the closing of pores and micro-fracture. The difference in the change in strength, porosity, permeability, and elastic and bulk modulus recorded for the rocks used in the research reviewed may be due to the nature of the original rock and the minerals [115,123], the nature of the pore fluid [115], physico-chemical condition [88,100,117] and the duration of chemical interaction between CO_2–brine–rock [127]. Pimienta et al. [95] found that dissolution of minerals in CO_2–brine increased with residence time, and Olabode and Radonjic [121] noted that with a long time of exposure, precipitation of minerals became dominant over dissolution in shales saturated with CO_2–brine. The duration of CO_2–brine residency is a very important factor that deserves more research.

Undissolved and mobile CO_2 is predicted to be in the reservoir for thousands of years [128]. However, most experiments have been completed within days or weeks, due to experimental limitations. It is necessary to determine the resident time needed for the different Phase CO_2–brine to have an impact on the properties of the rocks. Peter et al. [109] saturated samples of rocks with different Phase CO_2–brine for 7 days and concluded that the impact of the resulting CO_2–brine on the properties of the rock started gradually from the first day and increased as the concentration of the acidic brine increased. Pimienta et al. [95] studied the effect of residence time on the dissolution and integrity of rocks flooded with CO_2 and found that the pore brine acidifies just after 2 h of exposure leading to calcite dissolution, a significant increase in the calcium ions of the brine concentration and commensurate changes in rock physical properties such as porosity and permeability. In a $scCO_2$ fracturing experiment, Zou et al. [129] observed that the CO_2–brine–rock reaction occurs rapidly (less than 0.5 h). Olabode and Radonjic [121] had reported a substantial change in the pH of effluent from shale flooded with CO_2–brine only after 3 days of flooding; the change in pH of the effluent was higher in the earlier days. Results from Pimienta et al. [95], Peter et al. [109]; Zou et al. [129] and Olabode and Radonjic [121] are short-termed and show that the impact of CO_2 on the properties of rock starts immediately and progresses with time. There is a need to carry out a long-term investigation. Hangx et al. (2015) and Espinoza et al. (2018), used samples from natural CO_2 analog sites, and provide insights into the long-term effect of CO_2 on rocks. Both studies report a reduction in strength and agreed on the role of cement size alteration as a control for chemo-mechanical changes, the dissolution of cement led to an alteration of cement size and consequent increase in porosity, reduction in strength, vertical compaction, and lateral stress. However, the conditions at CO_2 analog sites may not apply to geological CO_2 storage. This review indicates that CO_2–brine–rock interaction is site-specific as the process can be easily affected by many factors that are bound to be different at different reservoirs.

Supercritical CO_2 is the most popular phase of CO_2 that has been used in geological storage research. This is because CO_2 is injected in supercritical conditions into the reservoir. Given the dynamic pressure-temperature condition of the reservoir, the phase of CO_2 will change; therefore, there is a need to investigate the impact of other phases of CO_2 in geological CO_2 storage. Peter et al. [94] and Peter et al. [109] evaluated the effect of different Phase CO_2–brine on deformation rate, deformation behavior, bulk modulus, compressibility, strength, stiffness, porosity, and permeability of reservoir rocks. Changes in pore geometry properties, porosity, and permeability of the rocks under CO_2 storage conditions with different Phase CO_2–brine were also evaluated using digital rock physics techniques.

Microscopic rock image analysis was also applied to provide evidence of changes in micro-fabric, the topology of minerals, and the elemental composition of minerals in saline rocks resulting from different Phase CO_2–brine that can exist in saline CO_2 storage reservoirs. In this paper, $ScCO_2$ refers to supercritical CO_2, whereas gCO_2 refers to gas-phase CO_2. It was seen that the properties of the reservoir that are most affected by the $scCO_2$–brine state of the reservoir include an increase in secondary fatigue rate, decrease in bulk modulus and shear strength, change in the topology of minerals caused by precipitation of fines, and agglomeration of grains, as well as change in shape and flatness of pore surfaces. The properties of the reservoir that is most affected by the gCO_2–brine state of the reservoir include an increase in primary fatigue rate, stress-induced decrease in permeability, porosity, and change in the topology of minerals. For all samples, the roundness and smoothness of grains as well as smoothness of pores increased after compression, whereas the roundness of pores decreased. Change in elemental composition in rock minerals in CO_2–brine–rock interaction was seen to depend on the reactivity of the mineral with CO_2 and/or brine and the presence of brine accelerates such change. Additionally, Lei and Xue [102] reported that the highest reduction in P-velocity and strength was seen in the sandstone sample saturated with supercritical CO_2 compared with those saturated with gaseous, liquid CO_2. These results show that the phase of CO_2 affects the nature of the impact of CO_2–brine on the properties of the rocks.

All CO_2 geological storage research that has been reported in this review is conducted under defined conditions and for a short time, different reservoirs have different conditions, and the condition of the reservoir changes over a long time, this imposes a limitation on experimental geological storage research as a slight change in reservoir condition can have far-reaching impact on the storage process. It is advised that CO_2 geological storage research be conducted as a dynamic process in which different possible scenarios can be examined. Additionally, CO_2 geological storage sites need to be explicitly studied and continuous monitoring of changes is recommended.

5. Trends in Geological Storage Research

Different experimental procedures have been used in past studies. Some researchers directly injected CO_2-saturated acidic brine into porous rocks [101,122,130], whereas some such as Yu et al. [131] have used synthetic rocks with CO_2 brine. Other researchers such as Zhu et al. [132] have used natural analog samples with CO_2–brine. On the other hand, Bemer et al. [133] used thermally activated acid instead of brine, apparently because CO_2 dissolution in water ultimately produces carbonic acid. The purpose of their experiment was to characterize the evolution of the properties of the rock induced by acid alteration. The merit of this method is the provision of information that helps monitor the evolution of the properties with a standard concentration of acid. Pimienta et al. [95] injected supercritical CO_2 in brine saturated rocks.

Irrespective of the procedure adopted, CO_2 and brine or a product of the reaction between CO_2 and brine must be in the reservoir rock. It is our opinion that natural rock samples taken from the proposed storage site are best for the prediction of the impact of geological storage research, as they are more representative. Samples taken from natural

analogs CO_2 sites and CO_2 storage sites are also useful for the understanding long-term impact of geological CO_2 storage.

Most researchers have investigated CO_2–brine interaction for the short term only. There is a dire need for the investigation of long-term CO_2–brine interaction. Most geological CO_2 storage research use laboratory core flooding experiments where samples are saturated with CO_2/brine. This is carried out under appropriate pressure and temperature conditions. The reservoir pressure and temperature conditions are simulated using high triaxial compression rigs, pressure vessels, and heating systems. Sometimes, imaging techniques such as computed tomography (CT) or scanning electron microscopy (SEM), X-ray diffraction (XRD), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), Brunauer-Emmett-Teller (BET), and Helium-porosimetry are included in the experimental setup. The injection of CO_2 is carried out using flow pipes in the flooding chamber. The temperature and pressure conditions that have been used in laboratory core flooding research range from 10–70 °C and 3–150 MPa, respectively. A summary of laboratory core flooding experiments performed by different researchers has been presented by Sun et al. [12]. Other important parameters necessary for the core flooding experiment include the core diameter, core length, temperature, and pressure as well as brine concentration.

Sun et al. [12], from a review of core flooding experiments around the world, presents this statistically. The optimum core diameter used in most core flooding experiments is 20–60 mm (79.3%), the core length is 50–150 mm (83.3%), the injection pressure is 10–30 MPa (95%) and the temperature is 40–60 °C (69.6%). Natural core samples are scarce; therefore, researchers will benefit from knowing the range of size of core samples that have been used in similar experiments to be aware of what size of the sample is appropriate, and the validity of the results. Most CO_2 core flooding experiments have been conducted with supercritical CO_2 while maintaining the pressure and temperature above 7.1 MPa and 31.1 °C, respectively. Aside from flooding experiments, percolation laboratory experiments can be used to study CO_2 geologic storage, the difference between percolation experiment and flooding experiment is the flow rate. Luquot et al. [134] used a percolation experiment to investigate the effect of flow rate and brine composition on CO_2 storage using CO_2-rich brine on Heletz reservoir rock samples.

Most experiments that have studied changes in rock properties as a result of progressive chemo-mechanical action of pore fluid in rocks have used water, supercritical CO_2, and/or brine as the pore fluid. The frequent use of water as pore fluid in research works is due to the assumption that pores contain mostly water. However, it is known that brine and hydrocarbon (when present) is contained in pores. With CO_2 sequestration, the stored CO_2 will also be contained in pores and will form a more complex mix [135]. Some researchers have studied the effect of CO_2 on different properties of rocks. However, the majority of such studies have used supercritical CO_2 and/or brine as pore fluids. This is because CO_2 is injected as a dense supercritical fluid.

Precipitation of salts and migration of fines is a phenomenon that must be looked at because it has great impact on the integrity of geological CO_2 storage. This leads to a change in the permeability, tortuosity, and porosity of the reservoir. Salt precipitation also affects the solubility of CO_2 in the brine as well as the chemical equilibrium in the system. Study on salt cavern by Maia da Costa et al. [32] has provided lead on this. This constitutes a potential threat to the efficiency of the system and researchers such as Yusof et al. [136] have studied injectivity impairment in sandstone due to salt precipitation and fines migration. Their result shows a direct correlation between salinity and change in injectivity due to precipitation of salt; the injectivity reduced by 26.7% from 6 when salinity changed from 6000 to 100,000 ppm. Higher salinity leads to a higher reduction in the injectivity, and the salinity of the CO_2 storage site will increase as mineralization progresses with time. To the best of our knowledge, this is the first of this kind of study, and more are needed to properly understand the effect of salt precipitation and fines migration on injectivity in different geological CO_2 storage scenarios. Pore scale studies are useful in providing more

understanding concerning micron scale phenomenon in rocks, example of such studies include [137–139] for shale, carbonate and bentonite-sand respectively.

6. Need for Future Study

It has been seen from previous studies that the effect of CO_2–brine on the strength, transport properties, and chemical composition of the reservoir has been fairly well investigated. However, less attention has been given to the effect of CO_2–brine on the pore and grain geometry properties of the rocks. Petrophysical, geomechanical, and transport properties of the rocks are controlled by the pore and grain geometry. Therefore, it is necessary to understand how CO_2–brine affects the pore and grain geometry properties, as this will enable better understanding, prediction, and modeling of changes in geomechanical, petrophysical, and transport properties of rocks in a CO_2 storage reservoir.

Firstly, more pore-scale numerical and laboratory experiments are needed to understand what happens at the field scale; thereafter, there can be upscaling of results from pore-scale studies to core-scale and field scales. In this regard, numerical simulation of CO_2–brine–rock interaction will be necessary because there are limitations in terms of the resolution and robustness of results in pore-scale laboratory experiments. This review focuses on the result of experimental studies, a review of complementary numerical studies is in progress.

Secondly, it is necessary to study a long-term prototype of geological storage to understand how the impact is affected by a long-term residency in the reservoir. The study of the samples or fields of CO_2 natural analog sites can also provide useful insights.

Thirdly, there is a need to carry out more studies to evaluate changes in the properties of reservoir rocks for the different Phase CO_2–brine states. Most researchers have used CO_2 in the supercritical phase with/without brine. This implies that only the effect of supercritical CO_2–brine is known. Given that reservoir conditions are variable and considering the solubility of CO_2 in brine, there will be resident undissolved CO_2 in the reservoir for a long time [109,140–145]. The resident undissolved CO_2 in a reservoir can change phase during the storage history. It is necessary to understand the difference in changes in the reservoir properties due to the different Phase CO_2–brine conditions.

There is a great need for future studies on CO_2–brine–rock interactions considering the phase of CO_2. This will improve the understanding of changes due to CO_2–brine–rock interrelationships and the accuracy of models/prediction of reservoir properties in geosequestration sites. Additionally, more experimental studies are recommended to understand the effect of different phases of CO_2 on the tertiary phase of fatigue in saline reservoirs as well as to investigate the role of pore shape and size on changes in rock properties in saline CO_2 storage sites.

Long-term geological storage experiments should be pursued. This is needed to provide an understanding of how CO_2–brine–rock interaction progresses with a longer period of residency of CO_2.

A major challenge with the study of CO_2–brine–rock is the scarcity of natural core samples from the depth that is suitable for storage. Therefore, there is a need to develop and conduct fluid–structure interaction (FSI) simulations using digital rock REV models. FSI is the interaction of deformable structures with the fluid that surrounds it; this will be relevant for evaluating changes in the properties of rocks surrounded by different phases of CO_2 and brine that could exist in saline storage reservoirs.

7. Conclusions

This review extends the understanding of CO_2–brine–rock interaction, highlighting new knowledge on the effect of the phase of CO_2 in geosequestration sites. It provides new elements that can help improve predictions of the effects of CO_2–brine–rock interaction on the physical, geomechanical, chemical, and petrophysical properties of reservoir rocks in huge saline CO_2 storage fields such as Sleipner, In Salah, and contributes to im-

proving storage integrity and ensuring CO_2 geosequestration support for the drive for net-zero emissions.

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