REVIEW ARTICLE

# Chemical Pre-Flush and Additive Strategies to Enhance $CO_2$ Solubility and Injectivity in Deep Saline Aquifers: Mechanisms, Evidence, and Field Readiness

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## Abstract

**Deep saline aquifers offer the largest global capacity potential for geologic carbon storage, yet storage performance is frequently constrained by coupled limitations on $CO_2$ dissolution (solubility trapping) and injectivity under high-salinity conditions. Elevated ionic strength suppresses $CO_2$ solubility via "salting-out" effects. Meanwhile, near-wellbore dry-out during injection of dry or undersaturated $CO_2$ can concentrate brine and precipitate salts, reducing permeability and injectivity. Mineralogy and $CO_2$-brine-rock wettability further control multiphase flow topology, interfacial area for dissolution, capillary trapping, and compatibility of additives with reservoir surfaces. This review critically evaluates chemical pre-flush and additive-enabled conditioning strategies intended to (i) increase local aqueous $CO_2$ dissolution capacity, (ii) mitigate or prevent dry-out-driven salt precipitation and near-wellbore formation damage, and (iii) enhance $CO_2$-brine contact through mobility control. We synthesize and compare evidence for four strategy families: (1) freshwater and engineered low-salinity (LoSal) pre-flush slugs and intermittent re-wetting; (2) chelating agents (e.g., EDTA/GLDA/DTPA) that complex multivalent cations and alter dissolution/precipitation pathways; (3) surfactant-derived $CO_2$ foams, including $CO_2$-soluble surfactants designed for foam generation at the displacement front with achievable injectivity; and (4) nanoparticle-assisted and hybrid foam systems that extend foam stability under harsh salinity and temperature.**

**Keywords**: deep saline aquifers, solubility trapping, salt precipitation, low-salinity pre-flush, chelating agents, $CO_2$ foam, $CO_2$-soluble surfactants, nanoparticles.

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## 1 Introduction

The rapid increase in atmospheric carbon dioxide ($CO_2$) emissions has emerged as one of the most pressing global challenges of the 21st century. Fossil fuel combustion, industrial activity, and land-use changes have disrupted the natural carbon cycle, causing greenhouse gas levels to rise at unprecedented rates [1]. Global $CO_2$ emissions reached over 37 gigatons in 2024, with China, the United States, and India being the largest contributors [2, 3]. This imbalance has already produced measurable consequences, including rising sea levels, melting polar ice, and more frequent extreme weather events [4]. While renewable energy deployment and emissions-reduction policies are essential, many decarbonization pathways also rely on CCS to address residual and hard-to-abate emissions [5]. Carbon capture and storage (CCS) is widely recognized as a complementary mitigation pathway, capable of providing immediate reductions while long-term energy transitions are underway [6, 7].

CCS involves capturing $CO_2$ from stationary sources and securely injecting it underground into suitable formations [8]. Several storage options are available, including depleted oil and gas reservoirs, unmineable coal seams, basalt formations, and deep saline aquifers. Each offers unique benefits, such as proven trap integrity in hydrocarbon reservoirs or dual recovery potential in coal seams [9, 10]. However, saline aquifers stand out for their global abundance, immense theoretical capacity, measured in thousands of gigatons, and spatial overlap with major emission sources [11–13]. Practical demonstration projects have underscored their viability. For example, the Sleipner project in Norway has safely stored approximately 20 million tonnes (Mt) of $CO_2$ since 1996 [14, 15], while the Gorgon project in Australia is one of the world's largest integrated CCS facilities, with a projected lifetime storage of 129 Mt [16]. Together, these projects highlight both the opportunities and the operational challenges of saline aquifer storage.

A key advantage of deep saline aquifers is the range of trapping mechanisms they support. Structural and stratigraphic trapping beneath impermeable caprocks provides immediate containment, residual trapping immobilizes $CO_2$ in pore spaces, solubility trapping dissolves $CO_2$ into brine, and mineral trapping converts it into stable carbonates [17–19]. Among these, solubility trapping is especially significant because dissolved $CO_2$ increases brine density, reduces buoyancy-driven migration, and establishes the conditions necessary for mineral precipitation [20, 21]. Long-term monitoring at Sleipner, for example, has shown that although only approximately 20-30% of injected $CO_2$ has dissolved into formation brine and less than 1% mineralizes, even this fraction plays a vital role in plume stabilization and injectivity control [14, 22]. Thus, improving solubility trapping directly strengthens the containment aspect of storage [23].

The effectiveness of solubility trapping is strongly influenced by pressure, temperature, and salinity [24]. High salinity reduces $CO_2$ solubility and promotes salt precipitation in the near-wellbore region, impairing permeability and injectivity [25–27]. In hypersaline systems, salt precipitation and early mineral precipitation can also reduce the pore volume available for dissolution [28, 29]. These issues compromise both short-term injectivity and long-term storage security. To mitigate such challenges, researchers have increasingly explored chemical pre-flush treatments, in which conditioning fluids are introduced into the aquifer before or during $CO_2$ injection to improve solubility trapping and minimize salt-related damage [30–32].

Several classes of pre-flush strategies have emerged to counter the effect of high salinity and enhance $CO_2$ solubility in brine. Freshwater or low-salinity injection can locally dilute brine and suppress salt deposition, as shown in simulation studies and at the Quest CCS project [26, 32, 33]. Chelating agents such as ethylenediaminetetraacetic acid (EDTA) and $N$,$N$-dicarboxymethyl glutamic acid (GLDA) can chelate multivalent cations, reduce scaling, and simultaneously accelerate carbonate mineralization [34–36]. Nanoparticles have been used to stabilize $CO_2$ foams, promote convective mixing, and modify wettability, with studies reporting up to 50% improvements in solubility trapping [37–39]. Surfactants, both water-soluble and $CO_2$-soluble, have shown promise in generating foams that enhance sweep efficiency and reduce gas mobility in saline aquifers [40–42]. Each method shows potential yet faces challenges related to cost, environmental compatibility, scalability, and reservoir heterogeneity [43, 44].

Despite encouraging laboratory findings, the real-world application of pre-flush treatments in CCS projects remains limited. Existing field-scale demonstrations, such as Sleipner and Gorgon, primarily rely on natural solubility processes, and deliberate chemical conditioning is uncommon in

**Table 1.** Selected geological $CO_2$ storage projects in saline aquifers [9, 45].

| Ref. | Project | Estimated storage capacity | Description | Implications for pre-flush treatment |
|---|---|---|---|---|
| [46] | Nagaoka field, Japan | ≈10 400 t injected (pilot, 2003-2005) | The Nagaoka pilot site is located in Niigata Prefecture, Japan. The project began in 2000, and $CO_2$ was injected between 2003 and 2005; the storage process used $CO_2$ and water injected in slugs. The site has a total depth of 1230 m, a storage thickness of 60 m, and handled injection rates of 20-40 t/day. | Water-alternating-gas (WAG) technique already acts as a built-in mitigation, so pre-flush is not considered. |
| [47] | Sleipner CCS, Norway | 25 Mt | Owing to the Norwegian carbon tax, $CO_2$ has been injected into the Utsira sandstone formation beneath an impermeable caprock in the North Sea at about 2800 t per day and approximately 800 m depth. The project showed that subsurface $CO_2$ storage can operate effectively without significant operational problems. | A freshwater pre-flush may be adopted should injectivity losses occur, but this has not been necessary so far, according to monitoring data. |
| [16] | Gorgon field, Australia | 129 Mt | The Gorgon CCS system on Barrow Island is one of the world's largest integrated capture and storage facilities. The project began in 2019 and has stored about 7 Mt of $CO_2$; cumulative storage is expected to exceed 100 Mt over its operational lifetime. Naturally occurring $CO_2$ separated from offshore gas reserves is injected into the Dupuy sandstone at depths of more than 2000 m. The storage interval lies about 2700 m below the surface with a thickness of 200-500 m, and the design injection rate is reported as 4.9 Mt per year. | Injectivity issues traced to salt precipitation may require a limited freshwater pre-flush or co-injection, if compatible with the clay structure, to avoid fines migration. |
| [48] | Jubail CCS Hub, Saudi Arabia | Up to 9 Mt/yr (Phase 1) | Joint venture (Aramco, SLB, Linde) aiming to be one of the largest CCS hubs in the region. | Pre-flush design depends entirely on characterization results such as salinity, mineralogy, permeability, and clay sensitivity. |

practice [49, 50]. Field-scale gaps highlight the need for a consolidated review that compares methods, evaluates feasibility, and identifies pathways for scaling from laboratory to industrial application. Given the scale of global $CO_2$ emissions and the focus on saline aquifers in CCS strategies, systematic development of chemical pre-flush techniques is necessary. Therefore, this review discusses key approaches, such as the injection of freshwater, chelating agents, nanoparticles, and surfactants, while emphasizing their mechanisms, feasibility, limitations, and connections to mineral trapping. By consolidating findings across experimental, modeling, and early field work, this paper provides a framework for selecting effective pre-flush treatments to maximize $CO_2$ solubility and ensure long-term storage security.

## 2 Saline Aquifers

Saline aquifers are among the most promising geological formations for large-scale $CO_2$ storage due to their widespread global availability, high storage capacity, and hydrodynamic separation from freshwater resources [51, 52]. Their high porosity and permeability facilitate the injection and migration of $CO_2$, while overlying impermeable caprocks (such as shale or mudstone) act as effective seals to trap the gas and prevent upward migration [11].

The global storage capacity of deep saline aquifers is estimated to be thousands of gigatons, significantly higher than that of depleted oil and gas fields or coal seams [12]. Furthermore, their wide geographic distribution allows $CO_2$ sources to be matched with nearby storage sites, reducing transportation needs. Operational projects such as Sleipner in the Utsira Sand formation (Section 1) have contributed significantly to understanding $CO_2$ plume behavior, geochemical interactions, and long-term containment mechanisms [15].

### 2.1 High Storage Capacity and Global Availability

Saline aquifers are expected to hold the largest $CO_2$ storage potential globally, far exceeding that of depleted oil and gas reservoirs or unmineable coal seams. Their theoretical capacity is measured in thousands of gigatons, sufficient to accommodate centuries of $CO_2$ emissions at current rates [53]. Moreover, these formations are spread worldwide, including regions where large stationary $CO_2$ sources are located, minimizing the need for long-distance transport [10]. Two techniques have been established so far to evaluate aquifer storage capacity, namely regional aquifer-based and structural trap-based

assessments [54]. The widespread availability of saline aquifers facilitates geographically distributed deployment of CCS. Their geological location also allows integration into existing energy infrastructure. Consequently, they form a key support to global strategies aiming to mitigate climate change through emissions reduction [13]. Some saline aquifers currently in operation and potential $CO_2$ storage sites are described in Table 1, along with their geographical description.

### 2.2 Suitable Geological Conditions for Supercritical $CO_2$

For effective and secure storage, $CO_2$ must be injected at depths exceeding 800 m to achieve a supercritical state. In this state, $CO_2$ exhibits properties of both gases and liquids-high density and low viscosity-which enhance both injectivity and storage capacity. At supercritical conditions, $CO_2$ occupies less volume and migrates more predictably through porous media [17]. Most deep sedimentary formations provide the necessary temperature and pressure conditions to support supercritical $CO_2$. Furthermore, storing $CO_2$ in this state reduces the buoyancy force that drives migration upward, improving containment under caprock layers. These thermodynamic benefits make deep saline aquifers particularly suitable for long-term geological sequestration [13].

Thermal conditions are equally important. Temperature typically increases by 25-35 °C per km, meaning most deep sedimentary basins naturally support supercritical $CO_2$ at depths of 0.8-1.2 km. Reservoirs located in tectonically active or geothermal regions may reach these conditions at shallower depths, whereas cooler basins may require deeper injection. The coupling of pressure and temperature also affects $CO_2$ density, which in turn governs buoyancy forces and plume migration rates. Higher reservoir pressures promote greater $CO_2$ dissolution into brine, lowering the risk of upward migration and facilitating solubility and mineral trapping [55].

Therefore, selecting an injection depth that ensures stable supercritical behavior while maintaining a safe pressure margin below the fracture threshold is critical for both operational efficiency and long-term storage security. Proper understanding of these pressure-temperature relationships allows accurate prediction of plume evolution, reservoir capacity, and the extent of solubility and mineral trapping during geological sequestration [56].

In deep sedimentary saline aquifers, formation-pressure gradients are commonly close to hydrostatic conditions. Representative literature-based values are approximately 9.0-10.0 MPa/km (1305-1450 psi/km), while reported minimum horizontal stress gradients are approximately 12.0-17.0 MPa/km (1740-2465 psi/km) [13]. These values are screening ranges compiled for deep sedimentary basins and should not be interpreted as universal values for all storage formations. They are most relevant to brine-filled sandstone or carbonate reservoirs at depths sufficient to maintain dense or supercritical $CO_2$ conditions, typically approximately 0.8-2.0 km, although the applicable range varies with basin temperature, lithology, stress regime, pore-fluid pressure, and burial history. Because they are literature-derived regional ranges rather than measurements from a single field or well, basin-specific pressure and stress data should be used when these values are applied to a particular storage site.

The difference between formation pressure and minimum horizontal stress provides only an initial screening indication of the available pressure margin. The actual allowable injection pressure must be determined from site-specific geomechanical and flow analysis. It is affected by capillary pressure and multiphase pressure losses, near-wellbore skin and permeability, wellbore and completion integrity, caprock strength and sealing capacity, fault orientation and reactivation tendency, reservoir heterogeneity, and pressure interference between wells. In addition, the minimum horizontal stress is not necessarily equal to the fracture pressure; fracture initiation depends on the complete in-situ stress state, rock strength, pore pressure, well trajectory, and perforation geometry [57]. Consequently, injection pressure should remain below a site-specific pressure limit established through pressure-transient analysis, well-integrity assessment, geomechanical modeling, and fault-stability evaluation rather than being selected solely from regional gradient ranges.

### 2.3 Rock Characteristics

Porosity and permeability are critical physical attributes that define the storage and flow capacity of aquifers. Porosity, typically ranging from 10% to 30% in sandstone aquifers and 5% to 25% in carbonate aquifers, determines the amount of $CO_2$ that can be stored [58]. Permeability, which may vary from

tens to thousands of millidarcies, controls how easily $CO_2$ can be injected and spread within the reservoir. Higher permeability facilitates higher injection rates, reducing the number of wells and associated infrastructure [59]. The heterogeneity in these parameters, especially layering and anisotropy arising from formation lithology, affects plume movement and residual trapping efficiency. Understanding these properties through site characterization and modeling is essential to designing and operating successful CCS projects [10].

However, these characteristics are only averages that downplay heterogeneity, which necessitates site-specific assessment [60]. Thin and low-permeability interlayers within the saline aquifer act as barriers to $CO_2$ migration, restricting its vertical and lateral spread in the formation and complicating accurate estimation of storage capacity [58]. Moreover, the porosity-permeability relationship could vary over time due to geochemical reactions from $CO_2$-brine-rock interactions. For example, salt precipitation can reduce permeability by up to 35% with only a slight change in porosity, while in other cases, permeability might unexpectedly increase due to mineral dissolution [27]. Such phenomena highlight the importance of modeling and empirical studies that cover anisotropy, layered heterogeneity, and evolving rock-fluid interactions to accurately predict injectivity, storage efficacy, and long-term integrity of storage projects [50].

### 2.4 Trapping Mechanism and Long-Term Stability

Saline aquifers provide several mechanisms to trap injected $CO_2$, enhancing both storage security and longevity. These include structural and stratigraphic trapping beneath impermeable caprocks, residual trapping due to capillary forces, solubility trapping as $CO_2$ dissolves into formation brine, and mineral trapping through geochemical reactions [17, 61]. While structural trapping provides immediate containment, solubility and mineral trapping offer long-term stabilization. Over time, $CO_2$ dissolves into brine, reducing its buoyancy and mobility, while reactions with formation minerals lead to precipitation of stable carbonates. These processes are particularly important in heterogeneous reservoirs where plume migration can be complex due to various interplaying forces. The presence of multiple trapping mechanisms is a major advantage of saline aquifers [13]. In addition to these trapping mechanisms, $CO_2$–rock geochemical interactions within the reservoir and at the caprock interface play a significant role in long-term containment security; such reactions alter porosity, permeability, and mineralogy over geological time scales, and their cumulative impact on storage integrity has been systematically reviewed for sedimentary rock systems [62]. The effectiveness of each trapping mechanism varies based on the geological and operational parameters of the aquifer, as summarized in Table 2, where the storage security is described over time, resulting from the factors responsible for storing $CO_2$.

**Table 2.** Comparison of $CO_2$ trapping mechanisms [51].

| Mechanism | Effectiveness | Stability and timescale | Key influencing factors |
|---|---|---|---|
| Structural trapping | High | High, immediate to long-term | Caprock integrity, fault presence |
| Residual trapping | Moderate | High, short- to medium-term | Pore throat size, $CO_2$ injection rate |
| Solubility trapping | Moderate | Very high, medium- to long-term | Water salinity, temperature |
| Mineral trapping | Low to moderate | Very high, long-term | Reactive mineral content, pH |

$CO_2$ in deep saline aquifers is subjected to a spectrum of trapping mechanisms that evolve over different time periods. Initially, structural and stratigraphic trapping, accompanied by impermeable caprocks and sealing faults, immobilizes the $CO_2$ plume and prevents buoyant migration [19]. Simultaneously, residual or capillary trapping begins to restrict $CO_2$ as disconnected droplets inside the complex pore network, which is influenced by the reservoir's wettability and pore-scale heterogeneity [18]. As time passes, residual trapping often becomes more dominant than solubility trapping, as the amount of residually trapped $CO_2$ may exceed twice the dissolved amount after several decades [63]. This shift is further regulated by temperature, pressure, aquifer thickness, and injection strategies, as thicker and high-pressure formations exhibit higher residual trapping during the post-injection period.

Solubility trapping reduces the buoyant tendency of $CO_2$ by dissolution in brine, resulting in increased fluid density and improved convective mixing. However, its efficiency is strongly dependent on brine salinity and composition [17]. High salinity can critically limit solubility trapping, which ultimately hinders the

transition to mineral trapping [21]. Although a slow process, mineralization plays a strategic role in the long term.

Importantly, solubility trapping directly sets the stage for mineral trapping. The more $CO_2$ that dissolves, the more carbonic acid is available to react with formation minerals such as Ca-, Mg-, and Fe-bearing silicates and carbonates. Thus, optimizing $CO_2$ solubility in the short term will accelerate carbonate mineralization in the long term, leading to more effective $CO_2$ storage by coupling the two mechanisms [64, 65]. Figure 1 shows a simple schematic of how trapping mechanisms are involved in immobilizing $CO_2$, starting from the less stable and temporary structural trapping prone to buoyant migration, to a more permanent form of trapping by mineralization.

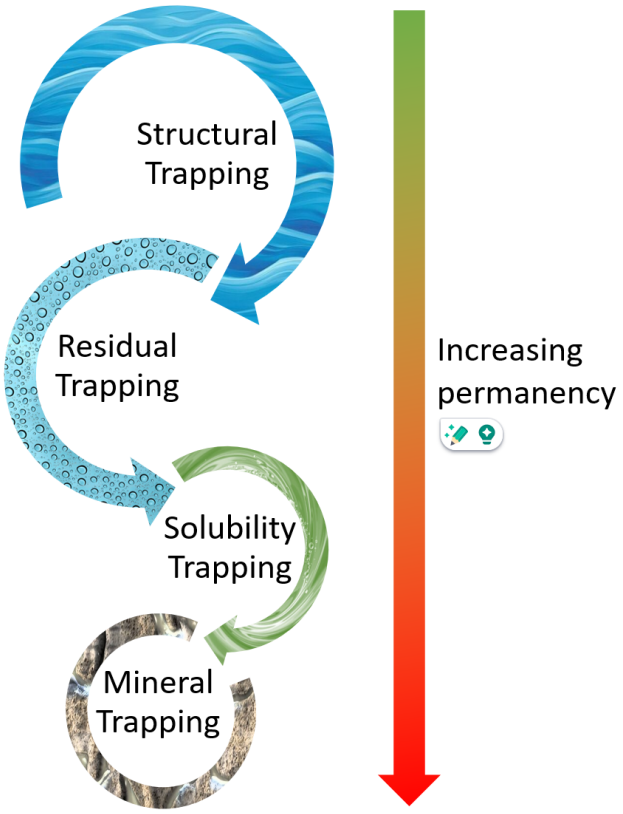


**Figure 1.** Contribution of different trapping mechanisms and permanency of storage.

The trapping mechanisms summarized in Table 2 apply broadly to both sandstone and carbonate saline aquifers; however, their relative significance varies with lithology. In sandstone formations, characterized by higher porosity, permeability, and mineral homogeneity, residual and solubility trapping dominate due to uniform pore connectivity and efficient $CO_2$-brine interaction [66]. Mineral trapping in such systems is slow due to the limited reactive mineral content. In contrast, carbonate formations exhibit greater geochemical reactivity, with abundant Ca- and Mg-bearing minerals promoting faster carbonate reactions once $CO_2$ dissolves, although heterogeneity and fracture-dominated flow can reduce residual trapping efficiency [67].

## 3 Factors Affecting $CO_2$ Solubility and Injectivity in Saline Aquifers

The impact of temperature, pressure, pH, and brine salinity on $CO_2$ solubility is crucial to predict and model the dissolution and precipitation of minerals, as these factors significantly influence the $CO_2$ sequestration processes [68, 69]. For example, an increase in pressure leads to greater $CO_2$ dissolution within brine, which then produces carbonic acid and triggers mineral breakdown [28]. Also, mineral dissolution takes place because of $CO_2$-induced pH variations, which alter the balance between precipitation and dissolution reactions [64, 67, 70]. Therefore, a fundamental understanding of these interdependent forces is necessary for developing $CO_2$ storage techniques within saline aquifers [71]. The study of these factors is essential to develop the most effective $CO_2$ storage project while incorporating enhanced measures to improve storage efficiency.

### 3.1 Effect of pH

Formation brine reacts with $CO_2$ to produce weak carbonic acid, lowering the pH of the system. In most deep saline aquifers, the original formation brine exhibits a near-neutral to slightly alkaline pH, depending on mineralogy and ionic composition [17]. This baseline arises from carbonate buffering reactions involving dissolved bicarbonate and hydroxide ions, which maintain near-neutral conditions before $CO_2$ injection [51, 70]. The acidic environment created by $CO_2$ dissolution allows carbonate minerals to dissolve, which results in greater formation porosity. In contrast, $CO_2$ exsolves during depressurization, which leads to an increased pH, resulting in carbonate mineral precipitation and a decrease in formation porosity and permeability [28]. The movement of injected gas affects how $CO_2$ dissolves and evolves from water, which modifies geochemical reactions. Figure 2 depicts a pore-to-reservoir scale schematic of $CO_2$ and mineral dissolution with and without depressurization [28]. Pressure strongly governs pH evolution within the aquifer. At high pressures, $CO_2$ remains dissolved as carbonic acid, creating acidic conditions that enhance mineral dissolution. In the

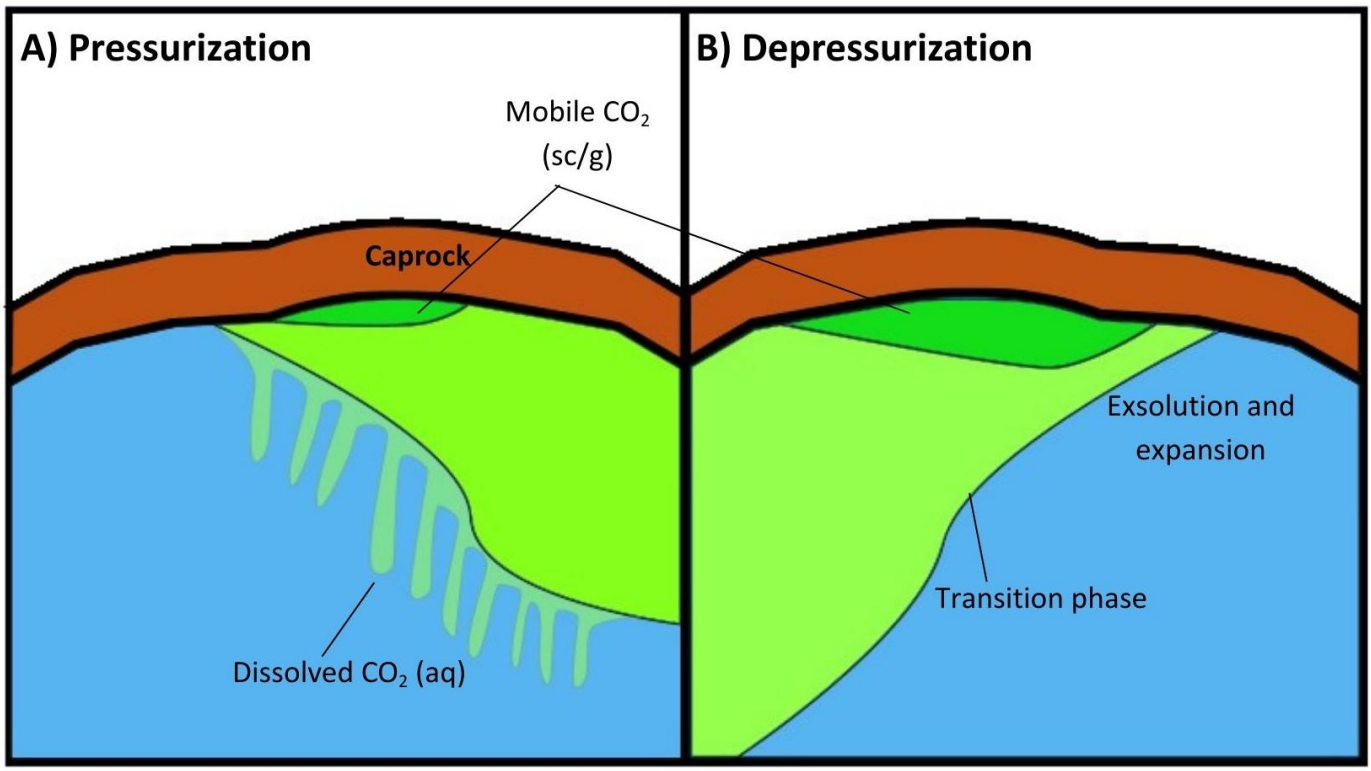


**Figure 2.** State of $CO_2$ after injection, undergoing geochemical activity, and the impact of pressure on trapping: (A) $CO_2$ without depressurization and (B) evolution with depressurization (modified from [28]).

event of leakage or abnormal depressurization of the aquifer system, $CO_2$ expands and exsolves from the aqueous phase [72]. Through this evolution, the chemical equilibrium between $CO_2$ and minerals is re-established, leading to an increase in pH and precipitation of minerals. Such geochemical reaction shifts result in variations of reservoir characteristics, such as porosity and permeability [28].

A study utilizing data from the upper Mt. Simon sandstone at the Illinois Basin-Decatur Project (IBDP) demonstrated this pH evolution through numerical reactive transport simulations [73]. The reported pH values were predicted by coupled geochemical and flow models that account for $CO_2$ dissolution, carbonic acid formation, and mineral equilibrium reactions, rather than measured directly in the wellbore. According to these models, the initial pH of 5.87 was predicted to drop rapidly to 4.45 following $CO_2$ injection and to 4.13 after 10 years of simulation, with the pH change confined to within approximately 100 m of the wellbore. This region is the most prone to $CO_2$-induced dry-out, which implies a coupled impact of pH on mineral dissolution and salt precipitation upon $CO_2$ introduction. Several studies indicate that low pH is responsible for greater calcite dissolution in unsaturated zones, and it is the major factor controlling the extent of calcite precipitation during $CO_2$ mineralization [51]. The variation in porosity and permeability due to $CO_2$ interaction is also limited to the regions where pH alteration took place [73].

### 3.2 Effect of Salinity

Formation brine containing high salt concentrations may promote salt precipitation in $CO_2$ injection zones, especially when the area near injection wells dries out. The reduction in formation porosity and permeability caused by salt precipitation negatively affects $CO_2$ injectivity. Salt precipitation risks can be reduced through freshwater pre-flush treatments that reduce the salinity of the brine, thus decreasing the chance of salt deposits [26]. Salinity significantly affects the solubility of $CO_2$ in brine. Typically, NaCl is the main salt present in saline aquifers, accounting for 70-90% of dissolved solids [74]. Because NaCl dominates the dissolved-salt inventory, it contributes most of the overall salting-out effect, although on an equal-molality basis divalent chlorides such as $CaCl_2$ and $MgCl_2$ impose a comparable or stronger salting-out effect owing to their higher ionic strength [69, 75]. At a microscopic level, this salting-out effect occurs because water molecules are highly polar and are strongly attracted to dissolved

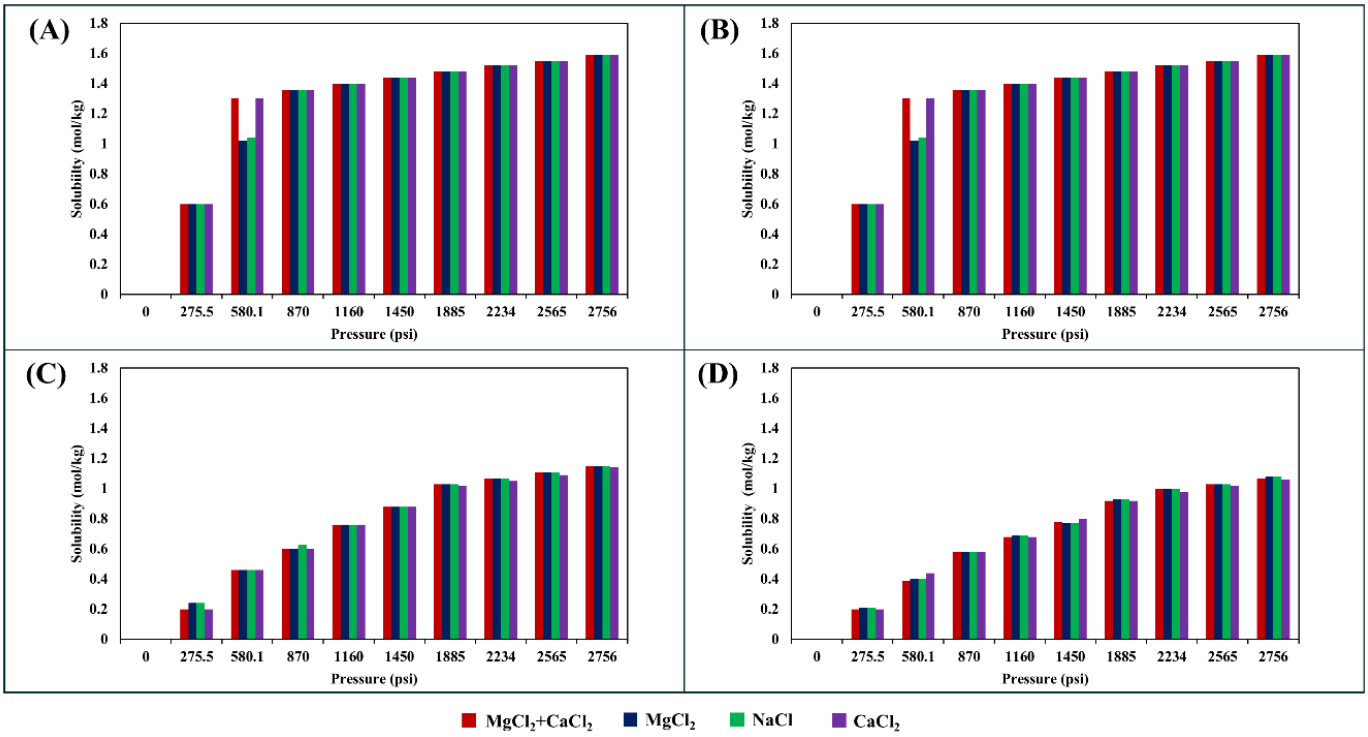


**Figure 3.** $CO_2$ solubility in 1000 ppm brines at (A) 25 °C, (B) 60 °C, (C) 80 °C, and (D) 100 °C, plotted from data reported in [76].

$Na^+$ and $Cl^-$ ions, forming tight hydration shells. Because many water molecules are occupied by these strong ion-dipole interactions, fewer "free" water molecules are available to interact with and accommodate the non-polar $CO_2$ molecules. As a result, $CO_2$ is effectively pushed out of the aqueous phase, significantly lowering its solubility. In addition, $Ca^{2+}$, $Mg^{2+}$, and anions such as $SO_4^{2-}$ alter activity coefficients and promote carbonate precipitation once $CO_2$ dissolves. Higher ionic concentrations further suppress solubility due to increased ionic strength [74, 76]. This is correlated with the different solubility trends shown in Figure 3, where the solubility of $CO_2$ in various ionic solutions of NaCl, $CaCl_2$, $MgCl_2$, and $MgCl_2$+$CaCl_2$ was determined at different temperature and pressure conditions. As observed, the solubility of $CO_2$ increased at higher pressures and decreased at higher temperatures. The experiments used a relatively low total salt concentration of 1000 ppm; therefore, these data are most representative of dilute brines and should not be directly extrapolated to highly saline storage formations [76].

Formation brine compositions are extremely important when mimicking aquifer conditions at the laboratory scale, as they dictate the extent and rate at which $CO_2$ dissolves in the brine [77]. It is important to note that brine concentration generally increases with reservoir depth [78]. Considering realistic salinity values while preparing brines is essential for designing conditioning treatments that achieve realistic and efficient results at the field level towards increasing $CO_2$ storage capacity. High salinity not only suppresses solubility but also delays the onset of mineral trapping by limiting the dissolved $CO_2$ available for geochemical reactions. Pre-flush methods that lower salinity can therefore enhance both solubility and the subsequent precipitation of stable carbonates.

### 3.3 Effect of Temperature and Pressure

Temperature and pressure play crucial roles in $CO_2$ sequestration by altering $CO_2$ solubility. These two parameters go hand in hand, and their effects are usually interdependent [79]. An elevated-pressure environment allows brine to absorb more $CO_2$ molecules, which transform into carbonic acid that dissolves rock minerals and enlarges pore spaces. Low formation pressure causes $CO_2$ to exsolve, which results in increased pH and the formation of carbonate deposits that diminish permeability [28].

Increased temperatures cause brine to become less accommodating of $CO_2$ molecules, thus hindering carbonic acid formation and reducing mineral dissolution rates. At higher temperatures, $CO_2$ solubility decreases because molecular kinetic

energy increases, reducing gas dissolution potential. Optimal conditions for solubility occur at high pressures (10-20 MPa) and low temperatures (below approximately 310 K, or 37 °C), as shown in Figure 3. Conversely, low pressures and high temperatures yield minimum solubility. Temperature elevation accelerates reaction rates, which may boost mineral dissolution and precipitation tendencies depending on the specific geochemical characteristics of the area [70]. Effective storage in saline aquifers requires a moderate range of subsurface temperature and pressure to preserve both injection rates and long-term stability. Deng et al. [80] determined $CO_2$ solubility in deionized (DI) water and two kinds of formation brine as a function of temperature and pressure.

Solubility rises with increasing pressure but decreases with higher temperature and salinity. The highest solubilization occurs in low-salinity or deionized water under high-pressure and low-temperature conditions, while solubility is most limited in concentrated brines at elevated temperatures and low pressures [80]. Comparable trends were observed in $CaCl_2$ and $MgCl_2$ systems, where solubility decreased with temperature, and differences relative to NaCl solutions were attributed to differences in ionic strength [75].

## 4 Pre-flush Treatment to Improve $CO_2$ Solubility

Efforts to enhance $CO_2$ solubility trapping revolve around conditioning the aquifer and increasing the contact between $CO_2$ and brine to speed up dissolution, and improving the capacity of the brine to hold $CO_2$ by altering its composition or the $CO_2$ phase behavior [81]. Pre-flush treatments refer to injecting a fluid or additive into the formation either before $CO_2$ injection (pre-flush) or alongside/after $CO_2$ injection (sometimes in cycles), to promote $CO_2$ dissolution and maintain injectivity [26]. This paper discusses several categories of conditioning treatment in the following sections, including injecting freshwater, low-salinity water, chelating agents, surfactants, and nanoparticles [82, 83].

### 4.1 Freshwater and Low-salinity Water Injection

Because high salinity is a major factor limiting $CO_2$ solubility, a logical technique is to inject low-salinity water into the aquifer before $CO_2$ injection to locally dilute the brine. By pushing out or diluting the brine around the injection zone, the $CO_2$ will first contact a fresh/low-salinity water phase, where it can dissolve more readily [30]. This strategy also has an immediate practical benefit, as it mitigates salt precipitation. LoSal water injection has previously been implemented to resolve halite formation issues near the wellbore and in the tubing of gas-producing wells [33]. When dry $CO_2$ is injected into saline aquifers, it tends to dry out the near-wellbore brine by evaporation, potentially precipitating salt and clogging pores. Freshwater washing was also used in the Quest CCS project to remediate halite deposition in $CO_2$ injection wells, where it improved $CO_2$ injectivity by up to 263% [32].

The main strength of this approach is its simplicity and strong mechanistic basis. Simulation studies and field experience consistently indicate that maintaining a less saline, water-rich near-wellbore region delays permeability loss and pressure build-up during $CO_2$ injection [26]. Compared with chemically more complex options, freshwater pre-flush does not depend on interfacial formulation stability or complex reaction pathways. It also integrates naturally with injectivity management because the same treatment that suppresses salt precipitation can increase the fraction of $CO_2$ entering the dissolved phase. In addition, lower salinity can promote convective mixing and improve the transition from structural or mobile $CO_2$ to more stable dissolved and residually trapped phases. For these reasons, freshwater or engineered low-salinity injection is generally the most field-ready option for reservoirs where salt precipitation is the dominant near-wellbore risk [31].

In field applications, a low-salinity pre-flush could be implemented by diverting some produced water (if of low salinity) or treated seawater into the injection well before starting $CO_2$ injection. Additionally, injecting freshwater before $CO_2$ helps remedy permeability loss and salt precipitation [25]. It was further proposed to add 3% butyl glycol to freshwater to eliminate halite precipitation in wells, although with unsatisfactory results [33]. Figures 4 and 5 compare the simulated salt concentration profiles for dry $CO_2$ injection without and with a freshwater pre-flush, respectively [25]: the pre-flush lowers and delays the development of the salt-saturated zone near the wellbore, although a saturated zone still develops after prolonged injection. Alternatively, co-injecting water vapour (steam) with $CO_2$ to keep the near-wellbore region humidified has been considered, but the energy required for compression and heating imposes significant environmental and economic penalties.

Beyond injectivity and dissolution, freshwater or low-salinity water injection plays a role in modifying

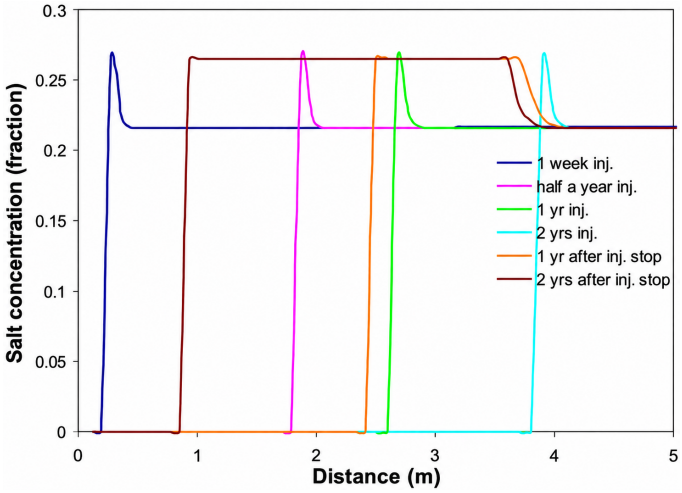


**Figure 4.** Salt concentration profile versus distance from the borehole after dry $CO_2$ injection without pre-flush (reproduced from [25]).

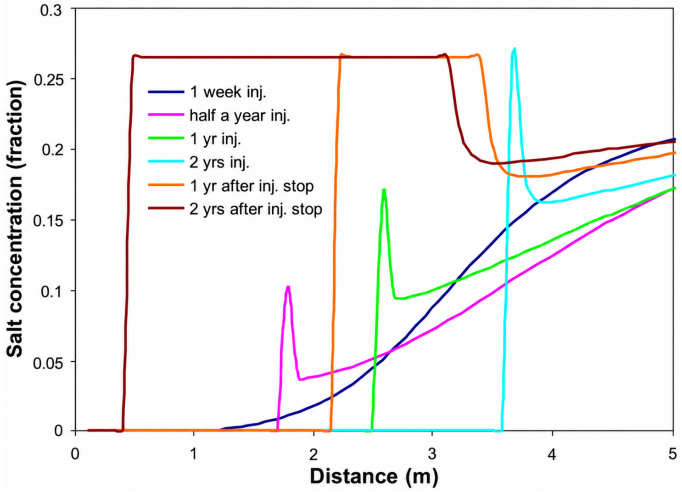


**Figure 5.** Salt concentration profile versus distance from the borehole after dry $CO_2$ injection following a freshwater pre-flush (reproduced from [25]).

the movement, mixing, and stabilization of $CO_2$ plumes. Because $CO_2$ is more soluble in low-salinity brine, a larger dissolved-$CO_2$ load produces a greater density increase relative to the ambient brine, thereby amplifying density-driven convective mixing and further enhancing the rate of $CO_2$ dissolution into the aqueous phase [71, 84]. Freshwater slugs also mitigate capillary end effects near the injection well. By sustaining water saturation, they suppress the development of dry-out zones where evaporative salt precipitation occurs [26, 50]. Hence, permeability is preserved and residual trapping is enhanced, as the retained water phase ensures $CO_2$ becomes immobilized as disconnected ganglia [63, 66]. Despite its ability to dilute formation brine and reduce salt precipitation, low-salinity water injection may introduce formation-damage risks in clay-bearing or fines-sensitive aquifers. A sudden reduction in ionic strength can increase the diffuse double-layer thickness around clay particles, promote clay swelling or dispersion, and weaken particle attachment to mineral surfaces. Mobilized fines may subsequently migrate and accumulate at pore throats, causing permeability reduction and injectivity impairment. The magnitude of this response depends on clay mineralogy and content, the initial brine composition, the concentration of divalent ions, pH, salinity contrast, injection rate, and the spatial distribution of low-permeability layers. Therefore, low-salinity pre-flushing should not be considered universally beneficial; the salinity and ionic composition of the injected water should be selected to minimize salt precipitation while maintaining rock-fluid compatibility. Site-specific compatibility tests, including coreflood experiments, effluent turbidity or particle analysis, permeability monitoring, and mineralogical characterization, are required before field application.

Importantly, freshwater and LoSal water conditioning can accelerate the transition from solubility trapping to mineral trapping. As more $CO_2$ dissolves, carbonic acid generation increases, promoting carbonate precipitation with divalent cations in the aquifer [20, 21]. In systems rich in reactive minerals such as feldspars or carbonates, this coupled process significantly boosts long-term storage security.

### 4.2 Chelating Agents

In recent years, the use of chelating agents to extract magnesium or calcium ions from silicate minerals to enhance mineral carbonation has been studied [36]. The injection of biodegradable chelating agents such as GLDA with seawater was found to be effective in improving rock porosity by dissolving surface-bound $Ca^{2+}$ and $Mg^{2+}$, which enlarges pore throats and improves flow connectivity. GLDA also led to an increase in mineral dissolution, enhancing the permeability and connectivity of pores for better $CO_2$ injectivity [35]. Owing to their ability to bind cations over a wide range of pH values, their use has extended to the extraction of these cations for industrial purposes and $CO_2$ mineralization. For instance, EDTA significantly enhances the extraction of Mg from serpentine, an Mg-rich mineral [85]. Moreover, GLDA-based fluids dissolve carbonate rock in a controlled manner at elevated temperatures, and their dissolution rate and wormholing behavior can be tuned through concentration and pH, which makes

it possible to balance acid-driven dissolution against secondary carbonate precipitation [86]. However, the efficiency of a ligand depends on its concentration and on the stability constant of the complex it forms with the target metal. For example, controlling $CaCO_3$ precipitation requires an appropriate chelant concentration and complex stability. For this case, at 25 °C and 0.1 M ionic strength, the stability constants ($\log K$) of the Ca-EDTA and Ca-GLDA complexes are 10.7 and 5.9, respectively [34, 87]. The higher the stability constant, the more strongly the ligand binds the metal ion [88]. However, to maintain rigor in the context of geological carbon storage, it is critical to account for actual subsurface conditions. Deep saline aquifers typically present much harsher environments, characterized by elevated temperatures (often 50-100 °C) and highly concentrated formation brines with ionic strengths far exceeding 0.1 M. Under these elevated reservoir temperatures and high-salinity conditions, the thermodynamic stability constants and overall binding affinities of these chelating agents will shift, generally reducing their effective chelating capacity. Consequently, the design of chemical pre-flush strategies must be carefully tailored to the specific environmental conditions of the target aquifer. In Figure 6, the working of GLDA as a biodegradable chelating agent is graphically depicted, explaining the steps from injection to carbonate mineralization.

It is crucial to consider the cation when choosing a chelating agent, as the stability of the chelated species depends on metal-ion properties. The greater the charge of the ion, the more stable the complex it forms with the chelating agent [89]. The potential to form complexes is determined by the charge and radius of the binding metal at the appropriate pH, as explained by Martell and Calvin [90]. Stability increases with $z^2/r$, where $z$ is the ionic charge number and $r$ is the ionic radius. The presence of d-orbitals is also crucial for the formation of stable coordination complexes, as transition metals are more likely to form chelate complexes [91]. For example, EDTA forms stable complexes with $Ca^{2+}$ and $Mg^{2+}$, but $Na^+$, being a monovalent cation with a single charge and weak electrostatic attraction, forms complexes of negligible stability with EDTA in solution. Moreover, chelating agents tend to form multiple bonds with a metal ion, which is possible only with multivalent cations. Therefore, chelating agents are preferred for extracting multivalent rather than monovalent cations [91]. The coordination chemistry of the binding chelant is crucial in treating different cations. Table 3 lists the stability constants of selected EDTA-metal complexes to indicate the binding strength of the ligand.

**Table 3.** Stability constants of selected cations with EDTA (25 °C, $I = 0.1$ M) [87].

| Cation | Stability constant ($\log K$) |
|---|---|
| $Fe^{3+}$ | 25.1 |
| $Cu^{2+}$ | 18.8 |
| $Ni^{2+}$ | 18.6 |
| $Pb^{2+}$ | 18.0 |
| $Zn^{2+}$ | 16.5 |
| $Co^{2+}$ | 16.3 |
| $Ca^{2+}$ | 10.7 |
| $Mg^{2+}$ | 8.7 |
| $Na^+$ | 1.67 |
| $K^+$ | 1.33 |

Alternatively, the ionic strength of the injected fluid must be carefully managed in clay-bearing formations. When the salinity of the conditioning fluid drops below a critical threshold—as may occur during chelant-assisted or low-salinity pre-flush operations—clay fines near the injection well can detach from grain surfaces, migrate through pore throats, and cause significant permeability decline and injectivity impairment [92]. This risk is further amplified in formations with high clay content or poorly cemented grains, where even moderate salinity reductions can initiate fines detachment and pore-throat plugging, underscoring the need for careful ionic-strength management during any pre-flush operation. Chelating agents also play a crucial role in accelerating mineral trapping. By releasing $Ca^{2+}$ and $Mg^{2+}$ from silicates and carbonates, chelants increase the availability of reactive cations that precipitate as calcite or magnesite once $CO_2$ dissolves [20, 21]. For instance, wollastonite dissolution was reported to be enhanced by chelating agents, leading to faster carbonate formation [36]. Other industrially available chelating agents are nitrilotriacetic acid (NTA) and diethylenetriaminepentaacetic acid (DTPA) [36].

However, challenges remain. High concentrations are needed for effectiveness, raising cost and environmental risks [93]. Chelants may mobilize trace metals and degrade under high salinity or temperature [89]. Field use has been limited to wellbore cleanouts rather than reservoir-scale deployment [94]. Future directions include green chelants such as GLDA that are biodegradable and effective under variable pH, and combining chelants with low-salinity injection to balance solubility and

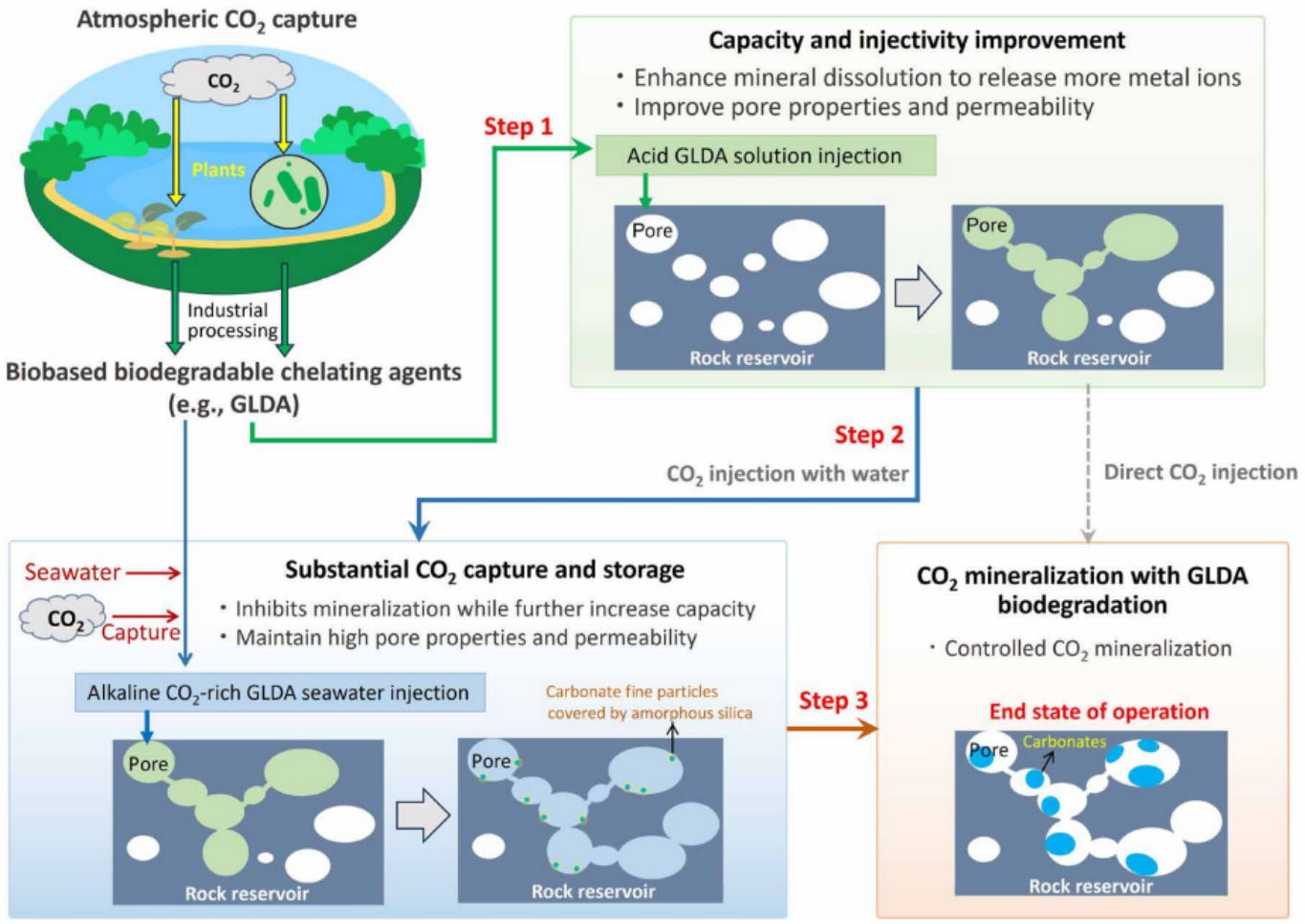


**Figure 6.** Mechanism of GLDA as a biodegradable chelating agent in $CO_2$ sequestration: (1) injection of GLDA to extract metal ions, (2) $CO_2$ dissolution and acidification, and (3) carbonate mineralization with GLDA biodegradation (reproduced from [35]).

mineralization [35]. These integrated approaches could bridge short-term injectivity improvements with long-term carbonate stability.

### 4.3 Nanoparticle-based $CO_2$ Injection

Nanoparticles (NPs) have emerged as a powerful tool in subsurface engineering due to their ability to modify fluid-fluid and fluid-rock interactions at the pore scale. For $CO_2$ sequestration, NPs can be used to stabilize $CO_2$-in-brine emulsions or foams, enhance convective mixing, and alter interfacial forces, all of which contribute to increased solubility trapping. Specifically, NP-stabilized foams, also known as Pickering foams, can disperse $CO_2$ into fine bubbles within brine, dramatically increasing the gas-liquid interfacial area and thus accelerating dissolution [37, 38].

Nanoparticle-based approaches have been investigated primarily as interfacial and mobility-control strategies rather than as direct chemical solubility enhancers. Across the available studies, their main contribution is to improve $CO_2$-brine contact by stabilizing foams, modifying wettability, and, in some cases, increasing the density contrast that promotes convective mixing [37, 38, 95]. Silica-based nanoparticles are the most consistently studied and appear to be the most practical because they can stabilize $CO_2$ foams under harsh salinity and temperature conditions, reduce gas mobility, and prolong gas residence time in the aqueous environment, thereby increasing the opportunity for dissolution [37]. More broadly, nanoparticle-stabilized foams have been shown to improve sweep efficiency, suppress viscous fingering, and produce more uniform displacement fronts than $CO_2$ injection alone, indicating that their storage benefit arises mainly from hydrodynamic control and interfacial stabilization rather than from a direct increase in intrinsic $CO_2$ solubility [38].

The literature also suggests that nanoparticle performance depends strongly on particle type and intended mechanism. High-density or heavy-metal

nanoparticles (such as Pb, $UO_2$, and steel) have been proposed as a means of accelerating convective mixing by increasing the density of the $CO_2$-rich phase. However, these must be strictly classified as theoretical exploration models. Owing to severe environmental toxicity and leakage-related concerns, they are not applicable to actual saline aquifer engineering. Such concepts remain purely theoretical and are far less practical than silica-based foam stabilization, which avoids these severe environmental and injectivity concerns [95]. In contrast, surfactant-nanoparticle systems appear more promising for storage applications because they combine foam stability with wettability alteration, often shifting the rock toward a more water-wet state and thereby improving capillary trapping in addition to dissolution [38, 66]. Overall, the comparative evidence indicates that nanoparticles are most valuable as supporting additives in mobility-control formulations, especially foam systems, whereas their direct use as standalone injectants remains less mature and less suitable for near-term field deployment [37, 38].

Recent advances employ surface-functionalized nanoparticles-for example, mesoporous silica or metal oxide NPs grafted with functional groups-to improve dispersion, reduce aggregation, and enhance interfacial stability under high salinity and temperature conditions (e.g., ethoxylated coatings, silane-modified surfaces) [96]. These tailored NPs serve as superior foam stabilizers in $CO_2$-brine mixtures, increasing interfacial elasticity, resisting coalescence, and extending foam life under harsh reservoir conditions [97]. Purification and redispersion techniques, such as solvent-free washing and supercritical $CO_2$ drying, have been explored to maintain NP stability after preparation, which is essential to preserve performance at injection scales [98].

Another emerging approach is combining NPs with nanobubbles, leveraging their synergistic effect on $CO_2$ dissolution and transport. Nanobubbles remain dispersed longer and increase the $CO_2$-brine contact area, while NPs assist in stabilizing bubble interfaces and enhancing mixing [39, 99]. Some preliminary modeling and laboratory results suggest that such hybrids can significantly enhance dissolution rates beyond what NPs or bubbles alone achieve. Importantly, NP-stabilized foams retained stability over several hours of injection and demonstrated the ability to reform after pressure cycling, a key requirement for field-scale efficiency [38].

Complementing experimental work, a comprehensive theoretical review and modeling study of nano-modified $CO_2$ injection was carried out by Rathnaweera and Ranjith [39]. Their work proposed that adding nanoparticles directly into the $CO_2$ stream (nano-$CO_2$) could accelerate convective mixing by increasing the density and viscosity of the injected fluid, thus altering the Rayleigh number and reducing the onset time of convection. Based on model predictions tested across 32 saline aquifer case studies worldwide, they found that nano-$CO_2$ injection could reduce the convective onset time by up to 80% and improve solubility trapping by around 50% relative to conventional $CO_2$ injection. They also highlighted that nanoparticles improve interfacial tension behavior, modify wettability, and minimize $CO_2$ mobility, which jointly enhance the stability and storage capacity of $CO_2$ in deep saline formations.

Despite these advantages, NP deployment faces hurdles: aggregation risks, injectivity concerns, high costs, and environmental compatibility [38, 100]. These limitations may become more significant during scale-up because heterogeneous formations can cause uneven nanoparticle transport and preferential accumulation in high-permeability channels or near-wellbore regions. Therefore, the improved foam stability observed in laboratory cores may not translate into uniform mobility control over field-scale distances. To date, no CCS project has applied NPs at the field scale, and the uncertainty associated with reservoir heterogeneity, fluid fingering, and long-distance additive transport remains a major barrier to field deployment. In terms of mineral trapping, NPs indirectly accelerate carbonation by maximizing dissolved $CO_2$ availability. Some metal oxide NPs (e.g., MgO, CaO) may even directly participate in carbonate formation under reservoir conditions, though this remains experimental [101].

### 4.4 Surfactant and $CO_2$-foam Injection

The use of surfactants to create $CO_2$ foams is a well-established technique in enhanced oil recovery. Foam reduces $CO_2$ mobility by forming a dispersion of gas within the aqueous phase, stabilized by surfactant molecules at the gas-liquid interface, and enhances solubility and residual trapping of $CO_2$ by extending residence time, increasing the gas-brine contact area, and distributing the $CO_2$ more uniformly through the formation. This reduction in mobility addresses a major challenge of supercritical $CO_2$: its tendency to

**Table 4.** Selected surfactants and their implications for $CO_2$ storage efficiency.

| References | Surfactant | Main contribution | Key limitations |
|---|---|---|---|
| [102, 103] | Zwitterionic betaine (e.g., cetyl betaine) | Forms stable $CO_2$ foams at high temperature ($\leq$150 °C) and salinity ($\leq$22 wt% TDS); improves mobility control and sweep efficiency. | Higher dosage may be required because of adsorption and partitioning losses; cloud-point precipitation and mineral adsorption may reduce propagation distance. |
| [104] | Nonionic ethoxylates (e.g., $C_{12\text{-}14}(EO)_{22}$) | Maintain foam stability at high temperature and salinity owing to a high cloud point; enhance in situ foam generation. | Require higher dosage; cloud-point precipitation risk; adsorption on minerals. |
| [40, 105] | $CO_2$-soluble surfactants (e.g., ethoxylated amines, $CO_2$-philic nonionics) | Generate foam in situ through the $CO_2$ phase; reduce mobility and improve sweep in carbonates. | Partitioning and adsorption losses can reduce surfactant concentration along the flow path; limited solubility in supercritical $CO_2$; possible handling or environmental concerns. |
| [38, 106] | NP + surfactant hybrids (e.g., silica NP + betaine/SDS) | Reinforced interfacial films give long-lived foams; enhance $CO_2$ dissolution and residual trapping. | Divalent-ion sensitivity, adsorption and retention on mineral surfaces, dispersion instability, and possible injectivity impairment at field scale. |

finger through brine and bypass large swathes of the formation due to its low viscosity and density.

Surfactant-based $CO_2$ foams are increasingly viewed as one of the most practical chemical strategies for improving storage performance in saline aquifers because they address a limitation that freshwater or chelating treatments do not directly solve: unfavorable $CO_2$ mobility. Across the reported studies, the main advantage of foam systems is their ability to redistribute $CO_2$ more uniformly, improve sweep efficiency, and increase gas-brine contact time, thereby enhancing both residual and solubility trapping [41, 42]. The literature also shows that foam effectiveness is not determined by surfactant presence alone, but by formulation quality, phase partitioning, and the ability to maintain foam strength under reservoir salinity, temperature, and heterogeneity.

A consistent finding across these studies is that stronger storage performance is obtained when foam propagation is balanced with injectivity and stability. High-dryness (ultralow water content) foam systems can provide strong plugging and mobility reduction, leading to deeper and more uniform sweep while lowering water consumption relative to conventional aqueous foam injection [103]. At the same time, comparative core-flood studies show that surfactant partitioning behavior is a critical design variable, since formulations that partition appropriately between $CO_2$ and brine generate earlier and more persistent foam, whereas poor $CO_2$ solubility or excessive stripping reduces storage benefit and accelerates foam decay [41]. This indicates that surfactant performance should be evaluated not only by foam strength, but also by resistance to stripping, adsorption losses, and the sustainability of foam propagation over multiple pore volumes. The distinction between conventional aqueous-phase surfactants and $CO_2$-soluble surfactants is especially important from a review perspective. Conventional surfactants can provide substantial mobility control, but $CO_2$-soluble surfactants offer an additional advantage by generating foam directly at the $CO_2$-brine interface within the formation, which improves propagation under continuous $CO_2$ injection and reduces phase-segregation problems [42]. This appears particularly beneficial in carbonate, layered, or heterogeneous systems, where in situ foam generation can improve sweep while avoiding severe injectivity penalties. Overall, the comparative evidence suggests that surfactant-based foams are among the most mature options for saline aquifer conditioning, but their success depends strongly on selecting formulations with appropriate partitioning, salinity tolerance, thermal stability, and adsorption behavior rather than on maximizing foam strength alone [41, 42, 103].

Surfactant adsorption on reservoir minerals is an important factor governing the field-scale performance and economics of $CO_2$-foam injection. Carbonate surfaces and clay-rich minerals can retain surfactant molecules through electrostatic, hydrophobic, or surface-complexation interactions, thereby consuming part of the injected chemical before it reaches the displacement front. Consequently, the required surfactant dosage and injection volume may be higher than laboratory estimates, increasing chemical procurement, mixing, transportation, and pumping costs. Adsorption can also produce concentration attenuation along the flow path, causing foam generation and mobility control to weaken with distance from the injector and limiting the effective transmission distance of the foam bank. However, adsorption is not necessarily detrimental in all cases. The adsorbed surfactant layer may alter rock wettability and interfacial properties, potentially promoting a more water-wet condition and enhancing residual $CO_2$ trapping. The net effect depends on mineralogy, surfactant type, brine salinity, pH, temperature, and the reversibility of adsorption. At longer times, desorption, chemical degradation, and redistribution of the surfactant may reduce foam stability and cause spatially variable wettability effects. Therefore, adsorption capacity and retention should be incorporated into formulation design, coreflood testing, foam-transport modeling, and economic evaluation rather than being treated only as a chemical-loss mechanism. Table 4 lists some surfactants and $CO_2$ foams that assist in enhancing $CO_2$ storage efficiency by improving mobility control and sweep efficiency, while simultaneously increasing residence time for gas-liquid contact.

Among the tested nanoparticles, silica ($SiO_2$) and surface-functionalized metal oxides (such as MgO and CaO) have shown the most consistent performance in enhancing $CO_2$ solubility and foam stability under reservoir conditions. Their hydrophilic or modified surfaces promote strong interfacial activity, improved wettability toward water-wet states, and stable dispersion at high temperature and salinity [37, 38, 96]. In contrast, heavy-metal or dense nanoparticles such as Pb, $UO_2$, and steel, though theoretically beneficial for increasing convective mixing due to higher density, present environmental risks, aggregation issues, and injectivity challenges, making them less suitable for large-scale application [95, 100]. Overall, silica and surface-modified oxides are considered the most practical nanoparticle options for enhancing $CO_2$ storage efficiency in deep saline aquifers.

Hybrid systems combining surfactants with surface-modified NPs are gaining attention. The NPs reinforce the elastic modulus of the surfactant film and reduce drainage, yielding more stable $CO_2$ foams under reservoir salinities [107]. In particular, novel NP coatings tuned for interfacial affinity have improved foam stability over extended durations, potentially enabling deeper penetration and longer residence times [97]. This synergy opens a pathway where surfactant foams are reinforced by NP frameworks, enhancing dissolution while maintaining foam robustness in subsurface operations.

Limitations of $CO_2$ foams include adsorption losses on minerals, salinity sensitivity, and degradation risks [44]. Economic and environmental factors, especially for large-scale projects, require further validation [43]. Foams strongly couple solubility and mineral trapping. By dispersing $CO_2$, they increase dissolution, while the extended residence time enhances carbonate precipitation with reactive minerals [28]. This dual mechanism makes surfactant foams one of the most practical near-term pre-flush strategies.

### 4.5 Comparative Evaluation and Mineral Trapping Integration

The comparative assessment of pre-flush techniques shows that each method enhances $CO_2$ solubility through distinct mechanisms and under different reservoir conditions. Freshwater or low-salinity injection is the most direct approach and has been field-tested as a remedial wash [32], reducing brine salinity and preventing salt precipitation near the wellbore. It may improve injectivity by preventing halite deposition, but it may also reduce injectivity through clay swelling or fines mobilization. Its selection should be based on the balance between these competing mechanisms rather than on salt-precipitation control alone. Chelating agents improve injectivity and promote mineral trapping by binding multivalent cations, though their cost and stability limit large-scale use. Nanoparticles modify interfacial behavior and enhance $CO_2$-brine contact, while surfactant-based foams control $CO_2$ mobility and increase sweep efficiency.

Hybrid systems, such as nanoparticle-surfactant or chelant-assisted low-salinity injections, combine these benefits to improve both dissolution and mineralization. The performance of each technique

depends strongly on formation mineralogy; sandstones favor solubility and residual trapping, whereas carbonates enhance mineral trapping due to higher reactivity. Overall, selecting an appropriate pre-flush method requires balancing injectivity, dissolution, and chemical stability to achieve secure and efficient $CO_2$ storage. From an engineering perspective, surfactant adsorption creates a trade-off between immediate chemical consumption and possible long-term wettability modification. Strong adsorption may increase the initial chemical requirement and reduce the distance over which foam remains effective, but the retained surfactant can continue to influence rock wettability after the mobile surfactant concentration has declined. This may improve residual $CO_2$ trapping, although excessive retention or degradation can reduce foam regeneration and lead to non-uniform treatment. Accordingly, the economic assessment should consider not only the unit price of the surfactant, but also adsorption-induced dosage increases, repeat injection requirements, water and mixing requirements, injectivity effects, and the incremental cost per tonne of $CO_2$ stored.

*Integration of pre-flush injection with mineral trapping.* All of these methods can accelerate the progression from solubility to mineral trapping by increasing $CO_2$ dissolution and carbonic acid formation, thereby enhancing geochemical stability. Hybrid approaches such as NP-surfactant foams or chelants with LoSal slugs may offer the most efficient solutions, balancing short-term injectivity management with long-term storage security. While each pre-flush method enhances solubility through distinct mechanisms, their long-term value lies in how they accelerate mineral trapping. Greater dissolution increases the dissolved inorganic carbon content, which drives carbonate precipitation. Thus, solubility optimization should be viewed not only as a short-term injectivity or storage efficiency measure, but also as a direct catalyst for geochemical stabilization in saline aquifers.

#### *4.5.1 Reservoir Heterogeneity and Scale-Up Uncertainty*

Results from nanoparticle-assisted foam experiments should be interpreted cautiously when extrapolating from pore and core scales to field-scale $CO_2$ storage. Laboratory cores are commonly smaller, more homogeneous, and less structurally complex than reservoir formations. In contrast, saline aquifers may contain layered permeability contrasts, shale or clay-rich interbeds, natural fractures, anisotropy, variable porosity, and spatial changes in mineralogy and wettability. These features can divert the injected $CO_2$-brine-additive mixture into preferential flow paths and create regions that are poorly contacted by the treatment. Consequently, the foam strength, nanoparticle distribution, and wettability alteration measured in a core may not be maintained uniformly over the much longer distance between an injection well and the reservoir volume.

Fluid fingering is an additional source of uncertainty during scale-up. Because $CO_2$ has a lower viscosity than brine and is affected by density differences, viscous fingering, gravity override, and channeling through high-permeability layers may occur. Foam can reduce these effects by increasing the apparent $CO_2$ mobility resistance; however, foam generation and stability may vary spatially because of surfactant adsorption, nanoparticle retention, salinity gradients, pressure changes, and local permeability. Fingering may therefore cause early breakthrough in preferential channels while leaving unswept or weakly treated regions between the channels. This reduces the effective transmission distance of the foam and introduces uncertainty in predictions of dissolution, residual trapping, and injectivity at the wellbore scale.

A rational scale-up methodology should therefore combine multiscale reservoir characterization with coupled flow and transport modeling. Relevant characterization includes core and log measurements of permeability, porosity, capillary pressure, mineralogy, fracture distribution, and wettability. These data can be incorporated into heterogeneous geostatistical models and evaluated using compositional foam-flow simulations that account for nanoparticle transport, adsorption, dispersion, retention, and foam collapse. Sensitivity analysis or ensemble simulations should then be used to quantify the effects of permeability contrast, layer thickness, fracture connectivity, injection rate, foam quality, and surfactant or nanoparticle concentration. Field pilots, tracer tests, pressure monitoring, and repeated coreflood experiments using heterogeneous or fractured cores would further reduce the uncertainty. Therefore, laboratory results should be regarded as evidence of mechanism and formulation performance, whereas reservoir-scale effectiveness requires validation through heterogeneous models and field-representative experiments.

## 5 Field Readiness and Application

Although freshwater or low-salinity pre-flushes are rarely documented in commercial $CO_2$ storage projects, modeling and experimental studies strongly

support their value in mitigating near-wellbore salt precipitation, a major risk to injectivity [26]. Numerical simulations indicate that pre-injecting a slug of freshwater before $CO_2$ can significantly reduce salt crystallization, preserving formation permeability during injection [25, 26]. These findings have been echoed in broader reviews, which show that salt deposition tends to cluster near the injection zone and can severely impair injectivity, even with minor porosity loss [29]. However, this method has not been implemented as a routine pre-flush in projects such as Sleipner, Snøhvit, or Aquistore. At Snøhvit, near-wellbore salt precipitation contributed to a rapid pressure build-up in the Tubåen Formation and required well interventions [108], illustrating the relevance of salt-related clogging and the potential value of pre-flush applications.

When it comes to chelating agents, nanoparticles, and surfactants, the field evidence remains sparse. Laboratory studies have demonstrated that chelants like EDTA can clean scale and prevent iron precipitation in wellbores, but these approaches are used primarily in oilfield maintenance, not in commercial saline aquifer storage [94]. Similarly, surfactants show potential: core-flood studies report that surfactants can increase $CO_2$ storage efficiency by helping generate foam or reducing interfacial tension, with improvements of up to 32% [109]. Yet, these remain confined to laboratory or simulation environments; their practicality at scale and compatibility with specific reservoirs are still being evaluated at the field level [43].

Finally, nanoparticles present an intriguing but still theoretical path forward. Some recent reviews argue that nanoparticle-augmented formulations (often combined with surfactants) may enhance $CO_2$ diffusivity, wettability control, and foam stabilization in harsh conditions, making them promising in concept for future field use [101]. Still, there have been no field CCS deployments of NP-based pre-flush or foam strategies. Interestingly, analogous trials in EOR contexts (such as nanoparticle-assisted $CO_2$ huff-n-puff pilots) have shown feasibility in oil recovery settings, but the relevance to $CO_2$ storage reservoirs remains to be demonstrated [100].

Lessons from field applications emphasize the need for cost optimization, particularly because adsorption losses may require additional surfactant volume or repeated treatment. The economic assessment should therefore include surfactant purchase, formulation and mixing, transport, injection, produced-fluid or residual-chemical management, and the cost associated with possible injectivity impairment or remediation. A formulation with a higher unit price may still be economically preferable if it has low adsorption, propagates over a longer distance, and maintains foam stability for multiple pore volumes. Hence, the relevant metric is the incremental cost per tonne of $CO_2$ stored or immobilized, rather than the surfactant price alone. Optimizing slug size, concentration, injection sequence, and surfactant-nanoparticle composition can reduce chemical losses while maintaining the required sweep and trapping benefits. Table 5 compares the economic aspects of different pre-flush methods and lists the influencing parameters.

## 6 Current Challenges and Future Prospects

Despite encouraging laboratory results, pre-flush techniques for $CO_2$ storage face substantial challenges when translated into field applications. The most immediate limitation is injectivity risk; while freshwater or low-salinity pre-flushes can mitigate salt precipitation, they may simultaneously destabilize clays or mobilize fines, leading to permeability loss rather than improvement [112]. Similarly, the use of chelating agents such as EDTA or GLDA is constrained by cost, large volume requirements, and potential geochemical side-effects, including mobilization of trace metals or alteration of mineral equilibria [113]. Surfactant-based foams, although effective in laboratory porous media, remain sensitive to reservoir salinity, hardness, adsorption, heterogeneity, and fluid fingering [114]. These effects can cause non-uniform foam propagation and early $CO_2$ breakthrough, making the prediction of effective sweep distance and storage improvement uncertain at the wellbore and reservoir scales. Similarly, nanoparticle-surfactant foams require validation in heterogeneous and fractured media before their laboratory performance can be considered representative of field behavior [38].

Looking forward, prospects for pre-flush methods in CCS are promising but hinge on careful site-specific design and incremental field validation. One avenue is the adaptation of intermittent or slug-based pre-flushes, where small volumes of LoSal water or surfactant solution are co-injected with $CO_2$, minimizing risks of clay swelling while maintaining injectivity [29, 30]. These clay-related risks should be evaluated during the initial design stage because

**Table 5.** Cost evaluation of different pre-flush techniques and their cost drivers.

| Method | Cost drivers | General cost range | Sources |
|---|---|---|---|
| Freshwater/low-salinity water injection | Pumping, sourcing, treatment, or desalination (especially offshore) | USD 0.5-1.5 per $m^3$ of treated seawater or desalinated water | [110, 111] |
| Chelating agents (EDTA, GLDA, NTA, DTPA, IDS) | Bulk chemical purchase, large dosages, possible degradation | USD 2-6 per kg (industrial grade); injection treatment typically requires several tonnes per well | [89, 94] |
| Nanoparticles (e.g., silica, metal oxides) | Synthesis, surface modification, stabilization, dispersion handling | USD 5-50 per kg (depending on NP type and purity) | [38, 39] |
| Surfactants/$CO_2$ foams | Surfactant purchase, injection, adsorption losses | USD 2-10 per kg (anionic surfactants); $CO_2$-soluble or specialized surfactants can exceed USD 10 per kg | [40, 43, 45] |

**Table 6.** Impact of geological formation type on chemical pre-flush strategies and $CO_2$ storage mechanisms.

| Reservoir characteristic | Sandstone formations | Carbonate formations |
|---|---|---|
| Mineralogy & geochemical reactivity | Predominantly quartz and silicates; generally low reactivity to injected fluids. | Predominantly calcite and dolomite; highly reactive with acidic fluids (e.g., dissolved $CO_2$, chelants). |
| Heterogeneity & flow mechanisms | Typically more homogeneous with uniform pore connectivity; dominated by matrix flow. | Highly heterogeneous; often features complex dual-porosity systems and fracture-dominated flow. |
| Dominant trapping mechanisms | Structural, residual, and solubility trapping dominate due to uniform sweep and limited reactive minerals. | Mineral trapping potential is significantly higher and faster due to abundant reactive Ca- and Mg-bearing minerals. |
| Pre-flush strategy focus | Enhancing solubility trapping (e.g., low-salinity pre-flush) and mobility control (e.g., nanoparticle-stabilized foams). | Inducing controlled mineral dissolution and providing mobility control to counter fracture channeling (e.g., $CO_2$-soluble surfactants, chelants). |
| Key risks of pre-flush fluids | Clay swelling, fines migration, and subsequent permeability impairment (especially with low-salinity water). | Rapid dissolution creating preferential flow channels (wormholing) and highly variable surfactant adsorption. |

the same salinity reduction that suppresses salt precipitation may destabilize clay minerals and mobilize fines. Another prospect lies in tailor-made surfactant and $CO_2$-philic formulations capable of tolerating extreme salinity and temperature, supported by recent advances in $CO_2$-soluble surfactants and environmentally friendly biosurfactants [115]. Nanoparticle technologies, particularly when combined with surfactants, are likely to play a role in enhancing wettability alteration and residual trapping but require pilot-scale demonstrations to confirm scalability [106]. Furthermore, integrated modeling and monitoring that link geochemical simulations, reservoir-scale foam propagation models, and geophysical surveillance will be essential to assess long-term stability and cost-effectiveness [40].

The geological formation type has a significant influence on both the efficacy and security of $CO_2$ storage when implementing chemical pre-flush techniques. In sandstone formations, high porosity and permeability promote uniform $CO_2$ distribution and efficient dissolution during freshwater or low-salinity pre-flush operations, with minimal mineral alteration risk [10, 59]. On the other hand, carbonate formations exhibit higher geochemical reactivity, where injected conditioning fluids such as chelating agents or surfactant-based foams can interact with minerals to modify pore structure through dissolution or precipitation, directly affecting long-term storage stability [21, 70]. In heterogeneous or clay-rich aquifers, pre-flush treatments must be applied cautiously, as low-salinity water or chelants

may mobilize fines or induce clay swelling, leading to permeability impairment [112, 116]. Therefore, the choice of pre-flush strategy should be closely aligned with formation mineralogy, clay content, and reactivity, ensuring that the method enhances $CO_2$ solubility and injectivity without compromising caprock integrity or geochemical stability [50, 117]. To systematically highlight how formation characteristics dictate the selection and success of chemical pre-flush treatments, a direct comparison of sandstone and carbonate reservoirs is summarized in Table 6. This synthesis underscores the necessity of tailoring pre-flush designs to site-specific geochemical and petrophysical conditions.

## 7 Conclusions

- Enhancing solubility trapping is critical for ensuring long-term $CO_2$ storage security in deep saline aquifers, as it directly supports both injectivity improvement and mineral trapping.
- Freshwater or low-salinity pre-flush is the simplest and most field-ready approach; it dilutes brine salinity, prevents salt precipitation, and enhances $CO_2$ dissolution and mineralization. However, its application must be formation-specific because clay swelling, fines migration, and permeability impairment may offset the injectivity benefits.
- Chelating agents (e.g., EDTA, GLDA) prevent scaling by binding multivalent cations, improve injectivity, and release reactive ions that accelerate carbonate precipitation, though high cost and degradation limit field use.
- Nanoparticle-assisted injection modifies interfacial and wettability properties to increase dissolution and stability, with potential for coupling with surfactants, but requires further field validation.
- Surfactant-based $CO_2$ foams offer the most mature technique for improving sweep efficiency and reducing gas mobility, thereby enhancing residual and solubility trapping under realistic saline conditions.
- Adsorption on carbonate and clay minerals may increase chemical consumption, shorten the effective foam-propagation distance, and cause spatially variable wettability alteration; therefore, adsorption behavior must be included in field-scale transport, stability, and techno-economic evaluations.
- The formation type and geochemical composition (sandstone vs. carbonate) govern pre-flush performance and storage permanence; strategies must be site-specific to balance dissolution, reactivity, and injectivity.
- Future work should prioritize scalability, cost efficiency, and environmental compatibility, integrating laboratory findings with reservoir-scale modeling and field pilot testing to validate pre-flush effectiveness.

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## Conflicts of Interest

Arshad Raza served as an Associate Editor of the *Reservoir Science* at the time of manuscript submission. To ensure the integrity of the peer-review process, Arshad Raza was not involved in the editorial handling, peer review, or decision-making process for this manuscript, which was handled independently by another editor. The remaining authors declare no conflicts of interest.

## AI Use Statement

The authors declare that no generative AI was used in the preparation of this manuscript.

## Ethical Approval and Consent to Participate

Not applicable. This article is a literature review and does not involve human participants or animals.

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