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# Mechanisms for geological carbon sequestration

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**Abstract**

The reduction of anthropogenic carbon dioxide ($CO_2$) in the atmosphere is crucial for mitigating the climate change. $CO_2$ capture and storage (CCS) is considered as one of the most promising options for carbon reduction. The main means is injection of $CO_2$ into structural reservoirs in deep, permeable geologic formations. The aim of this paper is to identify the main research needs and gaps in trapping mechanisms of geological carbon sequestration. Trapping mechanisms for geological sequestration include hydrodynamic trapping, solubility trapping, and mineral trapping. The properties of the $CO_2$-water/brine system as well as the hydrodynamics, geophysics, and geochemistry of the reservoir rock/fluid system are discussed.

*Keywords:* geological carbon sequestration, trapping mechanisms, reservoir rock

## 1. Introduction

Climate change is one of the most significant challenges of our time. Carbon dioxide ($CO_2$) and other greenhouse gas emissions are believed to be the cause of the major concern. The IEA study indicates that $CO_2$ emissions will increase by 130% by 2050 in the absence of new policies or supply constraints as a result of increased fossil fuel usage [1]. Carbon capture and storage (CCS) is considered as one of the most promising options and the only technology available to mitigate atmospheric emissions of $CO_2$ from large-scale fossil fuel usage [1, 2]. Deep saline aquifers, depleted oil and gas fields, and unminable coal seams are the primary targets for the geological storage of $CO_2$.

In recent years, fundamental research has focused increasingly on the short and long term effects of $CO_2$ injection into reservoirs to assess the feasibility of $CO_2$ storage on a commercial scale. Sequestration processes involve different trapping mechanisms according to the hydrodynamic, physical and chemical conditions in the formation. It is common to divide these mechanisms into four different categories: hydrodynamic trapping, residual trapping, solubility trapping, and mineral trapping.

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Another major concern of all storage options is the sealing efficiency of low-permeable sequences (caprock) overlying potential storage reservoirs. It has been suggested that any technology used to geologically store $CO_2$ underground should store it for a minimum of 1 000 years with a leakage rate of less than 0.1% per year [2−4]. The sealing capacity and long-term integrity of caprock, considering different kinds of mechanisms, is therefore an important issue for site approval and public acceptance [5]. Four different ways in which caprock can fail have been identified: diffusive loss through the caprock, leakage through pore spaces when capillary breakthrough pressure has been exceeded, leakage through faults or fractures, and well leakage when wells are degraded or inappropriately abandoned. The caprock-sealing mechanisms are recently reviewed by Song and Zhang [6], and thus not discussed in this paper.

This paper addresses the mechanisms of $CO_2$ trapping in the geological formations. In doing so, it both highlights key research findings and critical gaps in the current literature. For each mechanism, a brief introduction, a description of the main mechanisms or dominant factors, and its effects for storage are presented. In the end, a comprehensive conclusion as well as a summary of research gaps and needs is given.

## 2. Trapping mechanisms

In terms of the pore space utilization, $CO_2$ is preferably injected in a supercritical state ($scCO_2$). This is because $scCO_2$ is denser than gaseous $CO_2$ [7]. $scCO_2$ may undergo a phase change due to changes in pressure and/or temperature. Depending on the reservoir conditions, $CO_2$ can be stored as compressed gas, as liquid, or in a supercritical phase. Most of the injected $CO_2$ will reside in a mobile phase of $CO_2$, free to move laterally or migrate vertically towards the caprock. Trapping of $CO_2$ as residual gas occurs when formation water encroaches or invades the $CO_2$ plume [8]. It will also dissolve partially into the aqueous phase, leading to solubility trapping, and it can react with native minerals, resulting in mineral trapping. These trapping mechanisms are discussed in the following subsections.

### 2.1. Hydrodynamic trapping

Hydrodynamic trapping refers to that $CO_2$ is trapped as supercritical fluid or gas under a low-permeability caprock. Carbon dioxide, being less dense than the formation fluid, will rise buoyantly until it encounters a caprock that has a capillary entry pressure greater than the buoyancy or hydrodynamic force. $CO_2$ will accumulate in such a structural or stratigraphic feature that has both vertical and lateral seals. Trapping by such a seal is called structural or stratigraphic trapping, or hydrodynamic trapping. This mechanism is very important in that it is a prerequisite for any storage site because it prevents the leakage of $CO_2$ through the caprock during the time required for other trapping mechanisms to come into effect [9].

For such trapping mechanisms, the trapping efficiency is determined by the structure of the sedimentary basins, which have an intricate plumbing system defined by the location of high and low permeability strata that control the flow of fluids throughout the basin. There are numerous variations of structural and stratigraphic traps, or combinations of both structural and stratigraphic traps that can be physical traps for geological $CO_2$ storage. Common structural traps include anticlinal folds or sealed fault blocks (Fig. 1). $CO_2$ can fill to the spill point until the breakthrough pressure is exceeded.

Structural or stratigraphic traps are mostly found in reservoirs that have held oil and gas for millions of years. In these reservoirs, storage capacity mainly depends on the volume of pore space. Hydrodynamic trapping has been recognized in saline aquifers of sedimentary basins that have extremely slow flow rates. A volume of carbon dioxide injected into a deep hydrodynamic trap may take millions of years to travel by buoyancy forces up dip to reach the surface before it leaks back into the atmosphere. For this traps,

storage capacity is affected by both the volume of pore space and the reservoir permeability [11]. $CO_2$ sequestration by this physical trapping mechanism depends greatly on the sealing capacity of caprock, making it a big challenge for site selection [6].
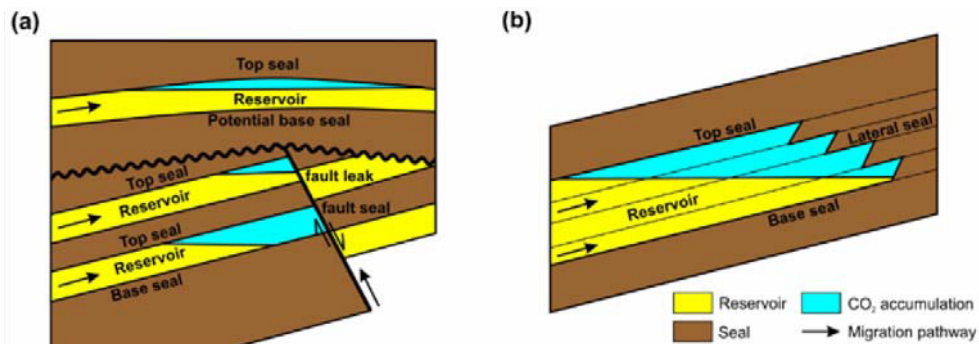


Fig. 1. Examples of (a) structural and (b) stratigraphic traps for $CO_2$ (modified from [10])

### 2.2. Residual trapping

When $CO_2$ is injected into the reservoir, it first displaces brine in a co-current fashion. But when the injection is stopped, due to the density difference between $CO_2$ and brine, the fluids flow in a counter-current fashion so that $CO_2$ migrates up towards and the brine flows downwards. Thus the wetting phase (brine) enters the pores by less-wetting phase ($CO_2$). In such a process, the brine displaces $CO_2$, leading to a significant saturation of $CO_2$ becoming trapped in small clusters of pores, see Fig. 2. The disconnected $CO_2$ is then trapped as an immobile phase. This trapping mechanism is called the residual trapping or capillary trapping.
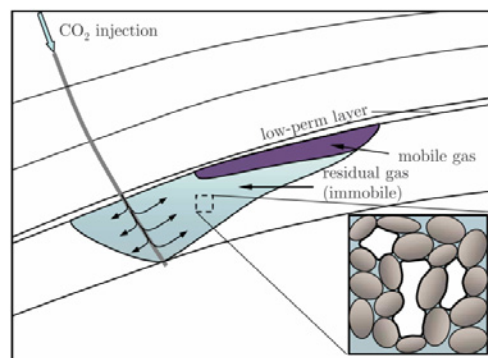


Fig. 2. Schematic of the trail of residual $CO_2$ that is left behind because of snap-off as the plume migrates
upward during the postinjection period [12]

The capillary trapping mechanism has a huge impact on the migration and distribution of $CO_2$ which, in turn, affects the effectiveness of the other trapping mechanisms. This has been shown with both experiments and numerical modeling results. Suekane et al. [13] experimentally evaluated the maximum trapped $CO_2$ saturation for typical conditions of aquifers at a depth from 750 m to 1 000 m. The trapped gas saturation is in the range from 24.8% to 28.2% for Berea sandstone core, despite the variation of $CO_2$ density, viscosity and interfacial tension. In addition, there are several simulation investigations

conducted to estimate the effect of capillary trapping. Two main approaches have been used in these studies of residual trapping behaviors [13]. The first isolates the effects of changes in relative permeability curves, calculating how trapped gas saturation change when the end point values such as critical gas saturation, residual gas saturation, wetting behavior, and irreducible water saturation are varied [12, 14−16]. Among these results, it is found that the residual trapping can limit significantly the movement of injected $CO_2$, resulting in a significant fraction of $CO_2$ trapping using a hysteresis model. They concluded that the effect of residual gas on $CO_2$ storage can be very large. The second approach makes use of various ratios of vertical to horizontal permeability ($k_v/k_h$), injection rates, formation pressure and temperature for a given set of relative permeability curves [17−19]. They found that the injection rate, heterogeneity, and the ratio of viscous to gravity force have the most significant impacts on the final immobilized saturation. Increasing the viscous to gravity force ratio and increasing the heterogeneity will enhance the sweeping efficiency, resulting in more $CO_2$ trapping as residual gas.

## 2.3. Solubility trapping

Solubility trapping refer to dissolution of $CO_2$ in formation fluid. $CO_2$ would migrate upwards to the interface between reservoir and caprock after injection and then spread laterally under caprock as a separate phase. When $CO_2$ contacts with the ambient formation brine and hydrocarbon, mass transfer occurs with $CO_2$ dissolving into the brine until an equilibrium state is reached. The solubility of $CO_2$ in water is dependent on the salinity, pressure and temperature of the formation water [20]. At the interface of free gas phase and formation water, $CO_2$ dissolves into water by molecular diffusion. The water in contact with $CO_2$ will be saturated with $CO_2$ and a concentration gradient of $CO_2$ would establish spatially. This process is very slow because the molecular diffusion coefficient is very small. It will take thousands of years for $CO_2$ to be completely dissolved in brine [21].

When diffusive $CO_2$ dissolves in brine, it slightly increases the brine density. The dissolution would increase the density of brine up to approximately 1% compared with the original formation brine [14, 22]. The heavier brine on the top of aquifer would flow downward due to gravity. Such convection enhances the mixing of $CO_2$ and brine and stimulates the diffusion process, following more dissolution of $CO_2$. The dissolution reduces $CO_2$ upward mitigation as well as increases the storage capacity. The crucial problem about the dissolution-diffusion-convection (DDC) process is the time and length scales of the onset of convection. Some approaches have been used for studying the onset of $CO_2$ convection in reservoir: amplification theory [23], global stability (energy) method [24], linear stability analysis [24, 25], and non-modal stability theory [26].

Modeling studies reveal that the DDC process can help to increase storage capacity in reservoir [27, 28]. Laboratory studies have been conducted that confirmed qualitative and quantitative aspects of it [29, 30]. Furthermore, as DDC process makes more $CO_2$ dissolve in brine, it is reasonable to expect that DDC may reduce the migration of $CO_2$ through caprock. It may be significant in storage capacity estimation and caprock sealing analysis.

## 2.4. Mineral trapping

Mineral trapping refers to the incorporation of $CO_2$ in a stable mineral phase via reactions with mineral and organic matter in the formation. Over time the injected $CO_2$ will dissolve into the local formation water and initiate a variety of geochemical reactions. Some of these reactions could be beneficial, helping to chemically contain or "trap" the $CO_2$ as dissolved species and by the formation of new carbonate minerals; others may be deleterious, and can actually aid in the migration of $CO_2$. It is important to understand the overall impact of these competing processes. However, these processes will also be dependent upon the structure, mineralogy and hydrogeology of the specific lithologies concerned [31].

Espinoza et al. [32] summarized representative chemical reactions and typical reaction rates in the literature, see Table 1.

Table 1. Mineral reactions with $CO_2$-acidified water

| Mineral | Typical reaction | Reaction rate (mol·m$^{-2}$s$^{-1}$) |
|---|---|---|
| Silicates [33] | $SiO_{2(s)}+2H_2O \leftrightarrow H_4SiO_4$ <br> $\leftrightarrow H^++H_3SiO_4^-$ <br> $\leftrightarrow H^++H_2SiO_4^{2-}$ | $1.26 \times 10^{-14}$ [36] |
| Aluminosilicates [34] | Anorthite: <br> $CaAl_2Si_2O_{8(s)}+8H^+ \leftrightarrow Ca^{2+}+2Al^{3+}+2H_4SiO_4$ <br> Kaolinite: <br> $Al_2Si_2O_5(OH)_{4(s)}+6H^+ \leftrightarrow 2Al^{3+}+2H_4SiO_4+H_2O$ | Anorthite: $1.2 \times 10^{-5}$ <br> Oligiocalse: $1.2 \times 10^{-8}$ <br> Albite: $3.6 \times 10^{-9}$ <br> Kaolinite: $10^{-14}$–$10^{-15}$ [37] |
| Carbonates [35] | $CaCO_{3(s)}+H^+ \leftrightarrow Ca^{2+}+HCO_3^-$ <br> $CaCO_{3(s)}+CO_2+H_2O \leftrightarrow Ca^{2+}+2HCO_3^-$ | Calcite: $1.6$-$3.2 \times 10^{-5}$ [38] |

The reaction rate of minerals in $CO_2$-water depends on temperature, pressure, pH, and concentration of other species. Besides the aqueous reaction, water-wet $scCO_2$ and dry $scCO_2$ reactions may occur when a large amount of dry $scCO_2$ flows through the reservoir. In this case, gradual displacement and dissolution of residual pore water occur and the rock comes into direct contact with dry $scCO_2$. Initial studies on dry $scCO_2$ or wet $scCO_2$ reactions have been conducted [39, 40]. The mineral dissolution is a very slow process as the reaction rates are usually very low and mineral trapping would only become significant at a geological time scale.

### 2.5. Summary

### 2.5.1. Relevant terminology

There are different relevant terminologies associated with $CO_2$ sequestration mechanisms. Definition for each one may be a little different in different literature, see Table 2.

Table 2. Mainly relevant terminology definition in the literature

| Terms | Definition and references |
|---|---|
| Static trapping | Mobile $CO_2$ is trapped in stratigraphic and structural traps, or in man-made caverns [41]. |
| Structural trapping | Structural traps refer to geological media which precludes the upward and lateral movement of $CO_2$ induced by crust movement (faults and folds) [41]. |
| Stratigraphic trapping | Stratigraphic traps refer to geological media which precludes the upward and lateral movement of $CO_2$ induced by depositional and/or diagenetic processes [41]. |
| Hydrodynamic trapping | (1) The buoyant $CO_2$ is kept underground by an impermeable caprock [9]. <br> (2) The injected $CO_2$ is primarily trapped as a gas or supercritical fluid. $CO_2$ will rise up due to buoyancy effect until it approaches the seals [42]. |
| Capillary trapping | (1) It means the trapping by capillary forces in the pores on the trailing edge of the mobile $CO_2$ plume (typically) [43]. <br> (2) $CO_2$ phase is disconnected into an immobile (trapped) fraction (or called residual trapping) [12]. |

| Residual trapping | (1) $CO_2$ can be stored as an immobile form in deep saline aquifers due to the petrophysical property of flow phases. $CO_2$ will be left behind as trapped (residual) saturation [14]. |
|---|---|
| | (2) $CO_2$ is trapped in the pore space at irreducible gas saturation in which case $CO_2$ is immobile because of the interfacial tension between $CO_2$ and formation water [41]. |
| | (3) It means the trapping by capillary forces in the pores on the trailing edge of the mobile $CO_2$ plume (less commonly) [43]. |
| | (4) Residual trapping happens when water is imbibed behind the migrating $CO_2$ plume, and is caused by gas-water relative permeability hysteresis [44]. |
| | (5) Formation of disconnected blobs of $CO_2$ phase is held by capillary forces [45] |
| Solubility trapping (dissolution trapping) | (1) $CO_2$ dissolves in water and/or oil [42]. |
| | (2) $CO_2$ dissolves in formation water, residual oil, or mixing with residual gas [43]. |
| | (3) $CO_2$ dissolves in hydrocarbons or water contained in subsurface formations [44]. |
| | (4) $CO_2$ dissolves in brine as aqueous species [45]. |
| Mineral trapping | (1) $CO_2$ reacts with minerals and organic matters in the geologic formations to become a portion of the solid matrix [42]. |
| | (2) $CO_2$ is trapped by precipitation of carbonate-bearing mineral phases, such as calcite, magnesite, siderite, and dawsonite [43]. |
| | (3) $CO_2$ is trapped by the mineralization process of mineral dissolution and precipitation [44]. |
| | (4) $CO_2$ is trapped by precipitation of dissolved carbonate anions and metal cations as solids [45]. |
| Physical trapping | (1) $CO_2$ is immobilized as a free gas or supercritical fluid and a process depends on the available storage volume [41]. |
| | (2) Physical trapping (structural and stratigraphic trapping) refers to the buoyant phase trapped below a seal or within a structure that has vertical and lateral permeability barriers [43]. |
| Chemical trapping | $CO_2$ adsorbs onto organic materials contained on coals and shales, or dissolves in subsurface fluids (solubility and ionic trapping) [41]. |

### 2.5.2. Time scale

The timescales associated with each of the sequestration mechanisms are very different [46]. Hydrodynamic trapping occurs during the injection and would be a perquisite for other trapping mechanisms. For this trapping mechanism, the caprock integrity and high capillary pressure are the key factors. During and after a short term of injection, capillary trapping occurs when the displacement happens. In short to mid-term, $CO_2$ dissolves in brine and the solubility trapping occurs. In geological time, $CO_2$ would be trapped by mineralization. The timescales for the four trapping mechanisms are as follows:

$$t_{\text{hydro}} < t_{\text{capi}} \ll t_{\text{solu}} \ll t_{\text{reac}}.$$

### 2.5.3. Spatial scale

$CO_2$ plume distribution changes with time when different trapping mechanisms dominate. During the hydrodynamic trapping, $CO_2$ accumulates under the low permeability seal and migrates laterally along it. Capillary trapping occurs all along the flow pathway, especially when the pathway has a very small pore or throat. Solubility trapping can be found at the interface of gas phase and brine along the flow pathway and under the caprock. Mineral trapping changes with the mineral distribution. The identification of dominating trapping mechanisms and $CO_2$ plume distribution at different time is of great importance for both the storage capacity estimation and the risk assessment.

## 3. Research gaps and research needs

Hydrodynamic trapping, capillary trapping, solubility trapping, and mineral trapping are four main trapping mechanisms of geologic $CO_2$ sequestration. Some studies have been done to investigate these mechanisms. But there are still some relevant topics that should be further investigated:

The capillary pressure of caprock and the week point of the seal should be well investigated as it decides directly the injection pressure and then the storage capacity of hydrodynamic trapping.

The relationship between geochemical reactions and their impact on porosity and permeability should be investigated in the context of $CO_2$ storage.

Capillary pressure curves and relative permeability curves should be obtained by $CO_2$ flow experiments whereas such curves were usually transferred from Hg-porosimetry or hydrocarbon systems.

Experimental methods need to be developed for imaging rocks for reconstructing three dimensional geometrics, with which flow, mineral reactions, and transport in such rocks can be studied.

Continuous effort should be invested in determining adequate kinetic rates under storage relevant conditions and characterizing reactive surface areas as well as in developing methods on how to upscale laboratory results.

A procedure has to be developed or improved to measure saturation and pH in rocks under in-situ conditions in percolation experiments.

Efforts should be made to develop adequate equations of state and solubility models when other gaseous compounds are included.

## Acknowledgements

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