

Review

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A Review on Carbon Dioxide Sequestration Methodology

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Review

Carbon Dioxide Sequestration Methodology—A Review

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Abstract: Carbon subsurface storage (CSS) has already been recognised as a critical, urgent, and essential method for reducing anthropogenic CO₂ emissions and mitigating the severe effects of climate change. CSS is the last stage in the carbon capture and storage (CCS) cycle and is accomplished chiefly via oceanic and subterranean geological sequestration, as well as mineral carbonation. The injection of supercritical CO₂ into geological formations causes a disruption in the subsurface's existing physical and chemical conditions; changes can occur in the pore fluid pressure, temperature state, chemical reactivity, and stress distribution of the reservoir rock. This paper aims to present a comprehensive review on the current advances in CSS, particularly CO₂ storage methods and the challenges encountered during the implementation of each methods and analyses on how key uncertainties in CSS can be reduce. CSS sites are essentially unified systems; yet, given the scientific context, these systems are typically split during scientific investigations based on the physics and temporal/spatial scales involved. Separating the physics by using the system as a boundary condition is a strategy that works effectively for a wide variety of physical applications. Unfortunately, the separation technique does not accurately capture the behaviour of the larger important system in the case of water and gas flow in porous media. This is due to the complexity of geological subsurface systems, which prevents the approach from being able to effectively capture the behaviour of the larger relevant system. This consequently give rise to different CSS methods. A good CSS application method can further improve the efficiency of greenhouse gas emission and their environmental impact, promoting the process sustainability and helping to tackle some of the most important issues that human being is currently accounting, global climate change. Though this technology is already large-scale development for the last decade, some issues and uncertainties are identified. Special attention was focused on the basic findings achieved in CO₂ storage operational projects to date.

Keywords: aquifer; carbon subsurface storage (CSS); CO₂ Sequestration; environment; geological storage; carbon capture and storage (CCS)

1. Introduction

Previous studies have emphasized Anthropogenic CO₂ as well as other greenhouse gas (GHG) emissions that have indeed been recognised as the primary cause of global warming and climate change (MacDowell et al., 2013). The reports published by IEA 2016 and NASA 2017 confirmed that CO₂ concentrations in the atmosphere have risen from 280 ppm in the mid-1800s to approximately 404 ppm in 2016, resulting in a nearly 1°C increase in mean earth temperature above the pre-industrial levels. This temperature increase, which occurred just between 1901 and 2010, resulted in a 20cm increase in worldwide mean sea level (UK Met Office 2016). It is widely acknowledged that the average global temperature increase from pre-industrial rates must be maintained far below 2°C by 2100 in order to avoid catastrophic climate change disasters (IPCC special report 2005). As a result, the European Union and the G7 countries have set a goal of reducing GHG emissions by at least 80% from 1990 levels by 2050 (IEA 2009) and (ECF 2010).

Power plants and other energy-intensive sectors are regarded as significant CO₂ emitters and are required to reduce their produced CO₂ emissions substantially. The high carbon intensity of the power industry (World Nuclear Association) 42%, is due to the significant proportion of coal-fired

facilities in the worldwide energy supply. Furthermore, the development of shale gas in North America has resulted in an increase in coal production and exports from the United States. As a result, it resulted in a significant decrease in coal pricing, which in turn resulted in a greater proclivity for coal-based power generation (Hanak et al. 2015). Therefore, de-carbonization of the electricity and manufacturing sectors is critical to meeting emission reduction goals.

CCSI in 2011 provided evidence for Carbon Capture and Storage (CCS) as the most crucial method for decarbonizing the electricity and industrial sectors. It is predicted that CCS alone may contribute almost 20% of the decrease by 2050 and that excluding CCS can result in a 70% increase in the worldwide cost of meeting emission reduction goals (UK DECC 2012). Permanent CO₂ sequestration is the US-DOE United States Department of Energy's plan. USGS VSP Vertical Seismic Profile XRD (X-Ray Diffraction) is the final step in the CCS chain and could be implemented using a range of strategies, primarily mineral carbonation, oceanic, and underground geological storage along with saline aquifers, oil and natural gas reservoirs, inaccessible coal seams, and other geological porous media. According to Yamasaki (2003), the critical criteria of a viable CO₂ storage option are net CO₂ emission reduction, high storage capacity, long-term CO₂ isolation (at least several hundred years), acceptable cost and energy penalty, and little environmental effect. However, public acceptance/embracing is another essential element that may have a significant impact on the technology's adoption, Mabon et al. (2013).

Several reviews, including Bachu (2015), and (Bai et al. 2015), have addressed various features of CO₂ storage in the past. However, particular areas have yet to be addressed or thoroughly examined. Despite the fact that CO₂ storage is a technically established technique, further deployment is hampered by ambiguity and challenges related to estimating storage capacity, tracking verification and monitoring of CO₂ during and after injection, characterising potential injection-induced seismicity, and standardising storage evaluation criteria, and practical, ethical mechanisms. Furthermore, CO₂ storage is dynamic subject, and current success and growth must be examined and addressed as more information becomes available.

2. CO₂ Sequestration Methods

According to the IPCC Special Report from 2005, different CO₂ sequestration methods that could be use stored CO₂ include deep ocean, geological and mineral carbonation, several subterranean reservoirs formations alternatives does exist, including saline aquifers, depleted oil and gas reserves, unreachable coal seams, hydrate storage, and CO₂ inside improved geothermal systems, (Bachu et al. 2000), (Han and Winston Ho 2020).

2.1. Storage in Subsurface Reservoir Formations

The most workable sequestration option is underground geological storage system. The security of the CO₂ being stored, as well as the detrimental effects on the ecosystem, are some of the key points that set geological storage from CO₂ mineralization and marine storage. Figure 1 depicts various possible geological storage systems that are considered to be effective and would need further investigation for better understanding.

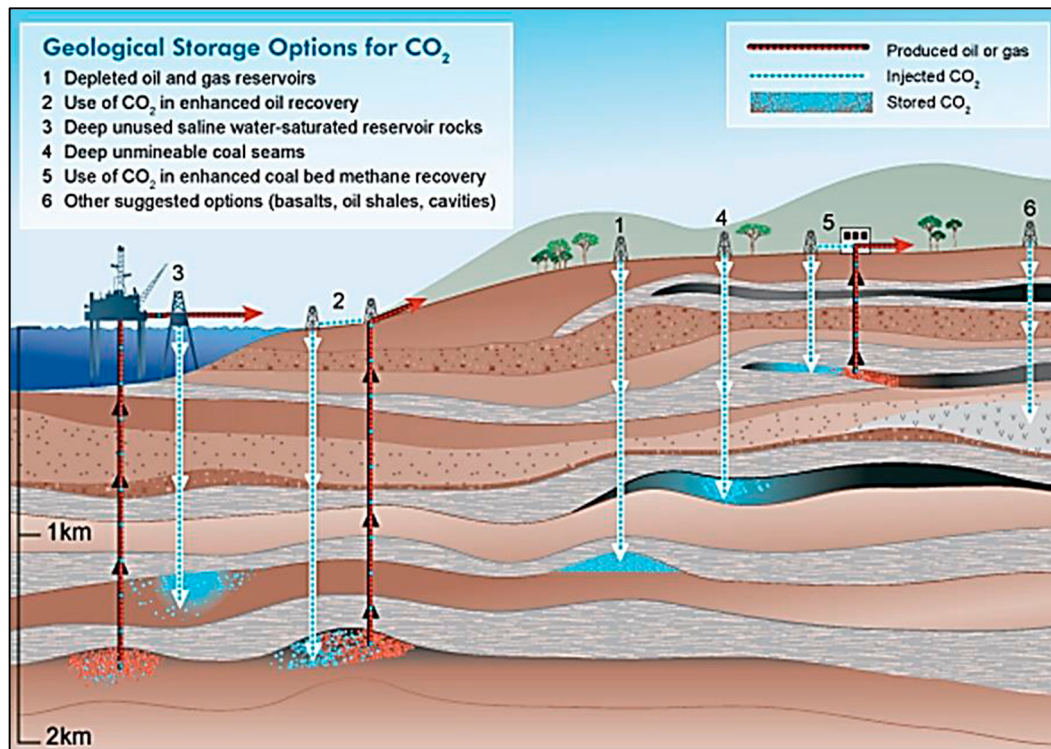


Figure 1. Schematic Illustration of Various CSS systems for CO₂ (Courtesy CO2CRC, 2015).

Considering that available information in the overwhelming CSS that can managed at the vast majority of locations in an efficient and safe way, there is still a possibility that storage facilities might be put in danger by factors such as generated seismicity if these factors are not well analysed.

2.2. Brine Aquifers

Several researchers have acknowledged that storing CO₂ in deep salty aquifers represents one of the most successful strategies for reducing CO₂ in the atmosphere (Li et al. 2023) (Javaheri et al., 2011), (Yang et al. 2013), (Frerichs et al., 2014), and (Burnol et al. 2015), due to its already available technological and significant possible storage capacity, (Bachu et al. 2000). However, most saline aquifers are presently unsuitable for other synergistic or competing uses (Trémosa et al. 2014) especially in highly populated nations (Procesi et al. 2013; Quattrocchi et al. 2013). The absence of facilities including wells for CO₂ injection, surface handling equipment, and transportation pipeline networks makes many salty aquifers less desirable as potential storage reservoir formation alternative at the moment (Li et al. 2006).

Recently, the topic of discussion has been the potential for CO₂ to be stored in salty aquifers (Bachu et al., 2003), (Wei et al. 2022) in combination with EOR storage (Boundary-Dam-Apache). These studies address topics including site description, as well as long term planning, according to (Bachu 2010) as well as the range of complementary and competing subterranean uses (Procesi et al. 2013).

Because of their vast pore volume and high permeability, aquifer reservoir formations can hold massive amounts of CO₂, cutting down on overall number of CO₂ injection wells required and easing pressure dissipation (Shukla et al. 2010). Upon flowing in to the storage reservoir formation, supercritical CO₂ dislocates brine in the pore spaces and initiates a chain reaction with the formation's minerals (groundwater, gas, and rocks) that lead to either formation of different chemical substances or breakdown of current minerals (Le Gallo et al. 2002), (Cantucci et al. 2009). Mineral formation and dissolution may alter rock porosity and, as a result, the capacity of the storage reservoir (Wdowin 2013).

Previous studies (Tapia et al. 2018) has shown that supercritical CO₂ has a density of approximately 0.6-0.7g/cm³ in saline reservoirs, the low density can influence the uprise movement of CO₂ towards the cap-rock because of buoyancy forces due to density variation.

According to previous studies (Armitage et al., 2013), a large aquifer storage basin with a high sealing capacity of the cap-rock is necessary for long-term and stable CO₂ storage. Given that cap-rock, a formation at the reservoir's top with low to very low permeability (Fleury et al. 2010) should operate as a seal to prevent CO₂ migration from the storage deposit below. With its low permeability, cap-rock is crucial for preventing CO₂ from escaping the retention reservoir and minimizing leakage. Another essential element that may result in cap-rock integrity loss and CO₂ leakage is the existence of unrecognised fracturing and fault-plane. However, from the review, no previous researcher has investigated further study in the impacts of CO₂-brine reactivity on injectivity and the fracturing network and fault plane for CO₂ storage, as such, a thorough research study is required to investigate the effect of this reactivity and previous faults on cap-rock stability (Buttinelli et al. 2011).

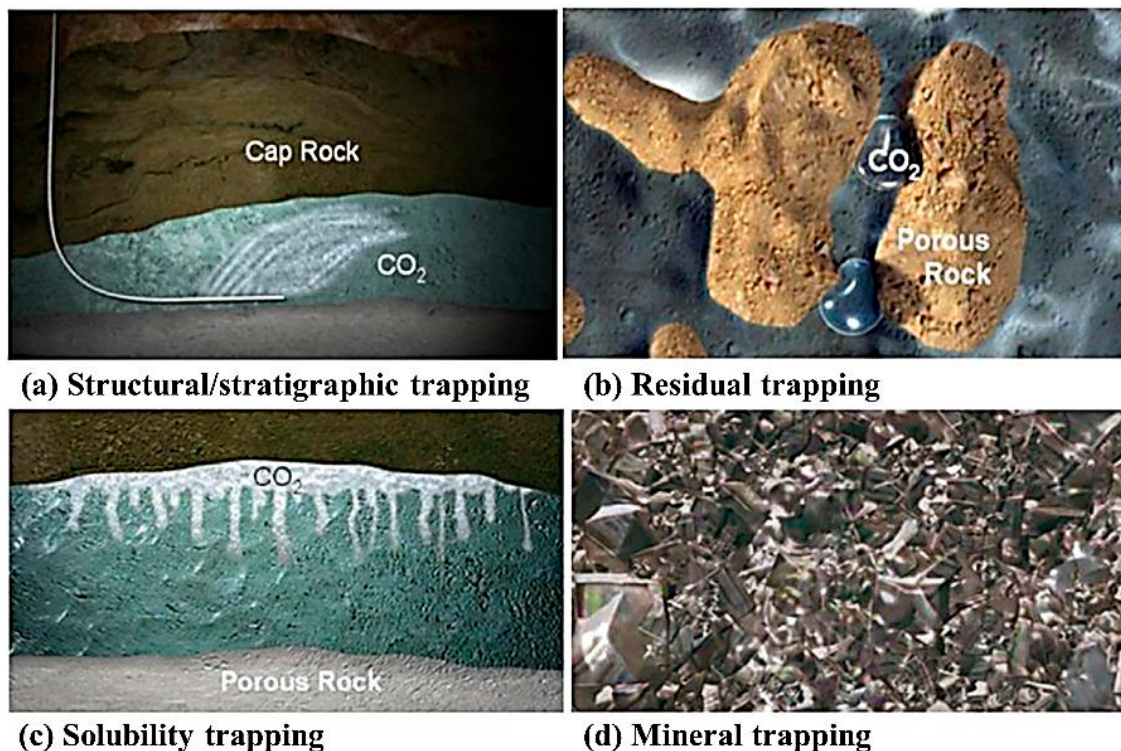


Figure 2. Illustrate the Major 4 CO₂ Trapping Subsurface systems (Zhao et al. 2014).

Figure 2 above depicts the four major trapping processes that may safely handle CO₂ storage:

- Structural/stratigraphic
- Residual
- Solubility
- Mineral trapping.

Stratigraphical and/or Structural Trapping: When CO₂ is introduced into a geological formation, it may move to the top and get trapped behind an impermeable top seal (Kim et al. 2017) where it can remain as a free phase that cannot go beyond or access the cap-rock pore region except by slow diffusion or fractures as illustrated on Figure 2a above. It's the most common kind of subsurface trapping system.

CO₂ Rock Pores Capturing: Injection of CO₂ into aquifer porous rock gives rise to fluid displacement due to differences in density. Figure 2b above shows how the fluid displaced by the CO₂ flows, returns, disconnects, and traps the remaining CO₂ within pore spaces. It has been observed that the method occurs exclusively when water drainage processes occur during CO₂ injection, rather than inside structural and stratigraphic traps, (Bachu et al. 2007).

Solubility trapping: CO₂ dissolves in brine through the chemical process of solubility, plummeting the quantity of CO₂ gas-phase (Figure 2c). Density of brine is increased by solubility of CO₂ and this may cause gravitational instability, hastening the transition of injected CO₂ to CO₂-lean brine (Kneafsey et al., 2010).

Trapping due to Mineral: CO₂ undergoes chemical interactions with minerals and salty water found around the rock's periphery. Carbonate precipitation occurs as a consequence of these chemical reactivity and has the effect of sequestering CO₂ in an inert lesser phase across a specific subsurface geological timeframe, as demonstrated in Figure 2d above (Bachu 1998). It is a more gradual process than the solubility capturing that takes place over a longer geologic time period (Gunter et al. 2004), (Sundal et al. 2014).

Although a number of studies have argued that storing CO₂ in salty aquifers would be more effective than CO₂ is often stored in depleted oil and gas fields, these assessments neglect to take into consideration the expenses connected as a result of the use of storage in saline reservoirs. In many instances, hydrocarbon fields already have production facilities in place, which, with only relatively modest adjustments, may be modified to meet storage operations. These changes can be made in order to accommodate storage activities. In addition, they have been well defined throughout the stages of crude oil exploitation, and they may employ CO₂ for storage as well as EOR. As a consequence, it is possible that storing CO₂ in hydrocarbon formations is better than storing it in saltwater aquifers.

2.3. Drained Hydrocarbon Reservoir Formations

The sequestration of CO₂ in depleted oil and gas reservoirs is widely recognised as one of the most efficient techniques of CO₂ storage. Among these advantages are the following:

- a. Drained hydrocarbon reservoirs have been the subject of substantial research both before and during the hydrocarbon exploring period, including research about their capacity for storage
- b. Both onshore and offshore infrastructural facilities, existing infrastructure, including CO₂ injection wells and transportation, may be used with little modification for the storage process (Sigman et al. 2021)
- c. If this was not the case, CO₂ gas injection to enhance oil recovery would have been less attractive and ends many years ago. Suitable hydrocarbon field's data as analogue may be utilise in illustrating the efficacy of cap-rock across geologic timeframe to strengthen oil and gas reservoirs (Heinemann et al. 2012).

Reservoir rocks and brine properties are similar and commonly found in both hydrocarbon reservoirs and deep aquifers storage system (Li et al., 2014). Oil and gas reservoirs, on the other hand, may be considered for EOR, making them more economically advantageous than saline aquifers, (Zangeneh et al. 2013) and (Gao et al. 2016). Because the worldwide average recovery factor from a typical oilfield is about 40%, (BGS, 2017), usually, many barrels of oil are still in the hydrocarbon reservoirs. It's the primary motivation for the global deployment of EOR. However, technological deployment difficulties remain challenging, although these issues may have been foreseen and handled throughout the exploration and production phase of a field, they have just recently come to light.

Gas injection is the most frequently utilised among the current EOR alternatives such as gas, thermal, chemical, and plasma-pulse injection techniques. Miscible gases (CO₂, nitrogen, and natural gas) are injected into the reservoir using the gas injection process to decrease the interfacial tension between oil and water and increase oil displacement efficiency while preserving reservoir pressure. CO₂ injection seems to be the optimal choice because it may reduce oil viscosity and is less expensive than liquefied natural gas (Jaramillo et al. 2008). More CO₂ for improved oil recovery is anticipate to be accessible from vital gathering point sources with the introduction of CCS technology (IPCC Special Report 2005). It has been claimed, for example, that the use of CO₂ for EOR has resulted in an increased output of about 260,000bopd in the U.S.A (GCCSI 2017).

The International Energy Agency (IEA) 2015 set out the following as the primary criteria for the implementation of CO₂ oil recovery support (EOR) projects:

- a. Additional site characterization involves investigating potential leakage risks, such as the condition of the cap rock and any abandoned wells with integrity problems.
- b. Additional evaluations of surface processing plants' fugitive and discharging emissions
- c. Leakage rates may be estimated from specific locations and the normality of the reservoir's behaviour can be determined by increased monitoring and field surveillance.

In addition to the criteria mentioned above, governments must address legal problems and enact laws to cover storage facility operations. These issues arise because CO₂-EOR and CO₂ permanent storage fall under two distinct regulatory umbrellas, the former focuses on resources recovery, whereas the latter is concerned with waste management Marston (2013). Legal issues might arise, for instance, regarding the proper decontamination of oil left in situ after production ceases, if hydrocarbon recovery is prioritised. Such a scenario may be jurisdiction-specific and especially significant when onshore mineral and storage rights are own privately.

One of the critical variables that must be rigorously define before a CO₂-EOR project is initiated involve the kind and number of contaminants in CO₂ streams. Depending on the CO₂ source and the accompanying collecting procedures, a variety of contaminants might be contained as part of CO₂ injection fluid. (Porter et al. 2015). The permissible impurities and concentrations are determined by a mix of transit, storage, and economic factors. CO₂ streams must meet a minimum purity standard of roughly 90%vol (Jarrell et al. 2002). In the case of CO₂, increasing impurity levels may cause the phase boundaries to move to even higher pressures, which demonstrates the requirement for higher injection pressures in order to keep the injected CO₂ in a higher concentration. It has also been established that non-condensable contaminants lower CO₂ storage capacity by a factor that is larger as compared to the mole percentage of contaminants present in the CO₂ injection system (IEAGHG 2011).

The most typical issue connected to contaminants is corrosion. Due to the corrosive effects that impurities (such as SO₂, NO₂, CO, H₂S, and Cl) may have on transportation and injection systems, it is essential to limit the quantity of contaminants on a scenario rationale. Additionally, it is essential to develop feasible mitigation solutions for potential problems, (Porter et al. 2015). It is important to note that even though certain impurities such as CO, H₂S, and CH₄ have a naturally occurring propensity to be combustible, safety considerations for combustibility are not typically factored into the evaluation of safety measures. This is because it is highly unlikely that the CO₂ injection stream will be combustible due to the low quantities of the impurities in question. Another issue that may influence the effectiveness of the CO₂-EOR process is an excessive concentration of O₂ in CO₂ streams. The presence of O₂ in the reservoir may stimulate microbial activity, (Porter et al. 2015), which can ultimately lead to operational problems such as injection obstruction, oil deterioration and oil souring.

The previous studies (Iggunnu et al., 2014) have connected environmental problems of EOR with volumes of water production that may include radioactive compounds and dangerous heavy metallic substance. Failure to implement an appropriate waste management and disposal strategy implemented, these chemicals may pollute drinkable water sources. Although restrictions exist, governments must ensure that operators follow current laws when brine re-injection for recovery is permitted. For example, White (2009) provided evidence to show that the Weyburn-Midale CO₂ storage project in Canada is an example of how collected in the Weyburn oilfield, CO₂ might be used for EOR and retention. Not only does this procedure recover a significant amount of previously unrecovered oil, but it also increases the oilfield's useful lifespan by 20–25 years, Thomas (2008). According to (Zaluski et al. 2016) ; (Verdon 2016) long-term surveillance, generated seismicity evaluation of CO₂'s impact on the reservoir and the fluids' mutual effect, oil and minerals have been the primary focuses of CO₂-EOR research (Hutcheon et al. 2016). The Weyburn case history inspired (Cantucci et al. 2009) to study the geochemical equilibrium between brine and oil and develop a biogeochemical model for CO₂ storage in underground reservoirs. A hundred years into the future, they predicted precipitation and disintegration processes based on research into reservoir formation

during CO₂ injection. During the first year of the simulation, they discovered that the two most significant chemical processes taking place in the reservoir were those involving CO₂ and the dissolution of carbonate. Furthermore, the development of chemical characteristics over time indicated that CO₂ might be securely stored via mineral and solubility trapping.

Perera (2016) acknowledges that though the CO₂-EOR method has substantially improved oil recoveries, further improvement is needed using the following strategies:

- a. Using numerical evidence, (Tenasaka 2011) proved that this was possible within the normal range of CO₂ injection. In the San Joaquin basin, scientists injected around 2.0HCPV (hydrocarbon pore volume) of CO₂ to prove that there was a greater possibility to extract more oil, almost 67% of the originally present oil (OOIP) was recovered. In addition, (Tenasaka 2011) demonstrated that there was a greater recovery of oil from his numerical methodology
- b. Using a better and innovative CO₂ flooding design and well management can positively influence more oil recovery from the reservoir
- c. Increasing the mobility-ratio by raising water's viscosity (Thomas 2008). Minimising miscibility pressure using miscibility-enhancing agents, Kuuskraa (2008).

2.4. In-accessible Coal Seams

An additional option for sequestering human-caused CO₂ is the use of inaccessible coal seams. Since cleats are present inside the coal matrix, the system is somewhat permeable. In addition, the matrix of coal is full of tiny holes (micropores) that may take in a lot of air. Coal has a greater affinity for CO₂ in the gas phase than methane, and this is the basis for the CO₂ trapping process. According to (Shukla 2010), this means that the methane output could be increased while the CO₂ was permanently stored. Thus, large amounts of CO₂ may be stored while commercial unconventional shale methane (CBM) processes are made more productive and profitable (Krooss et al. 2002), (Gilliland et al., 2013). It should be underline that although CO₂ increases CBM synthesis, the overall quantity of methane generated is not always higher than without the addition of CO₂. The International Energy Agency Working Group on Greenhouse Gases (IEAGHG 2009) provided an overview of the essential technical parameters needed for the effective implementation of enhanced coal seam production, which include:

- a. The homogeneity Reservoir
- b. Threshold of fractures and fault planes
- c. Upper depth limit
- d. Coal geomorphology
- e. Permeability adequacy

Two experimental locations, the Alberta Carbon Trunk Line (ACTL) in Canada with the San Juan Basin pilot in the United States, have reportedly used the ECBM approach, the conclusion of the evaluations for the Alberta project (Krooss 2002):

- a. Even in constrained reservoirs, continuous CO₂ injection is feasible.
- b. Injection may be performed notwithstanding a decrease in injectivity.
- c. Expected Significantly Enhanced CBM Production
- d. The injected carbon dioxide stays in the reservoir, boosting sweep efficiency, (Lakeman 2016).

Key findings from the San Juan Basin pilot study revealed that methane recovery exceeded the predicted ultimate primary production. Second, the pilot project was not cost-effective because of the price of gas at the time of it launched. However, if price of gas continues to climb in the years to come, the pilot project may end up being lucrative; thirdly, due to the fact that fuel prices were high when the project was first implemented, the trial project was not profitable. An additional pilot study of a Coal field is being done in Appalachian Basin, with a focus on a variety of surveillance and verification techniques, and accounting (MVA) methods are being utilised to understand better storage complexity, (Gilliland et al. 2012). Furthermore, the possible ECBM implementation, as well as the significant variations in output across nearby wells with the same stratigraphic, has been

studied in the beginning. However, further research is needed to characterise and portray such disparities adequately.

While CO₂ EOR has been used successfully for years in the upstream oil and gas sector, the utilisation of CO₂ during ECBM is still limited in its recognition. There are still many unknowns when it comes to ECBM recovery, however, the current understanding of how the CO₂ EOR process works could help alleviate some of those worries. For example, the creation of technically recoverable shale in ECBM could need a look at already-existing technology from the oil industry that might be converted with very little work. Existing well materials may be utilised as a baseline for good integrity in ECBM production following suitable changes. Furthermore, field and reservoir management techniques processes, such as risk monitoring and evaluation may be modified from those already in place and used at any point in the lifetime of a project.

2.5. Subsurface Basalt Formations

There exists a considerable body of literature on subsurface basalt deposits within central igneous provinces, and many researchers (McGrail et al. 2006), (Pollyea et al. 2014) and (Matter et al. 2016) have suggested subsurface basalt deposits as a possible CO₂ storage solution. Basaltic rocks make up around 8% of the continents and a large portion of the ocean bottom. As a result, basaltic rocks have a massive theoretical CO₂ storage capacity (Anthonsen et al. 2014). One of the most important advantages of such rocks' potential to store CO₂ is that their physical and chemical characteristics, as well as the amount of divalent metal ions they contain, may fix CO₂ during past geological periods (Van Pham et al., 2012). Permeability and porosity of Basalt flows, on the other hand, are very variable and often consist of an interior low-permeability region surrounded by periphery regions with high permeability. That said, the rubbly zones between separate flows are the most critical portions of a basalt sequence for CO₂ storage.

Complimentary CO₂ injected into subsurface basalts (the CarbFix pilot scheme, Iceland) may replace water in the rock's pore spaces and cracks (Matter et al., 2011). The decrease in water content may impede basalt carbonation and hydration. Therefore, it may be possible to inject CO₂ and the right amount of water into the same reservoir based on the following points:

- a. Because it offers sufficient depth, denser CO₂ liquid may sink, which delays the release of CO₂ back into the atmosphere
- b. It makes it possible to form stable carbonates in a shorter amount of time than would normally be required by geologic processes
- c. It prevents acidic basement fluids from rising via an impervious sediment layer
- d. It can be converted into a stable hydrate
- e. It is essential to remember that a small quantity of CO₂ leaking does not inevitably damage the sea bottom ecosystems.

Because of the anticipated development of dolomitic carbonate minerals, with the possibility of CO₂ being trapped in basalts for thousands of years, analysing changes in rock volume and the chance of fracture self-healing are key issues to consider. Quantitative research on such issues has been conducted (Van Pham et al., 2012). These researchers found out that at 40 degrees Celsius, oxide consumed a significant amount of calcium, limiting its use to the creation of siderite and ferromagnesian carbonates. Magnesite formed with ankerite and siderite at temperatures between 60 and 100 degrees Celsius. In addition, they found that the carbonation and hydration processes both increased solid volume and inhibited pore access, decreasing the maximum quantity of CO₂ stored.

In addition to studying the mineral assemblages present in basalt, researchers have looked at the mechanisms of mineral carbonation in serpentinites, with the intention of acquiring a more thorough comprehension of the fundamentals of CO₂ storage for the future utilising basic magnesium silicates. In serpentinites, rocks that are both plentiful and thermodynamically suitable for the production of magnesium carbonates, CO₂ combines with magnesium silicates to produce magnesium carbonates (Seifritz 1990). (Andreani et al. 2009) conducted an analysis of the carbonation process using flow parameters that were optimised. They found out that low-flow or low-diffusion

regions are the only ones where porosity and permeability decreases. In contrast, higher flow rates contribute in armouring of mineral surfaces associated with the initial disintegration.

And further reason for alarm has been the occurrence of fractures in the basalt formations' protective cap-rock. Due to the possibility of leakage via the fissures, basalts are not likely to be suitable for CO₂ storage. However, CO₂ seeping via fissures has the potential to mineralize and be trapped inside the formation, delaying its escape to the surface (IEAGHG, 2011). As such, further research is required to characterise the kinetics of CO₂-basalt interactions.

Alternate storage alternatives, including serpentinite and basaltic reservoir formations, could be necessary; knowledge improvement is required to identify possible uncertainties and investigate mitigation techniques. To do so, it may be necessary to apply computational techniques and to research the impact of carbon dioxide and rocks contact on the ease or difficulty of migration, as well as to clarify CO₂ migration in the presence of likely fault plane, fractures.

2.6. CO₂ Sequestration in Hydrate deep Formations

Previous studies (Anon n.d.) have shown that subsurface CO₂ storage system as hydrates is another potential, modern strategy that uses a lattice of water molecules to capture CO₂ molecules. When water and the right level of pressure and temperature are present, CO₂ hydrate may form rapidly (Circone et al., 2003). Furthermore, its rapid formation kinetics may allow for some self-sealing in the rare crack development in the hydrate top layer formation. The development of CO₂ hydrate might have applications in both underground geology and the storage of CO₂ in the ocean. Because the formation of hydrate turns to be very stable at higher pressure and low temperature of about 10°C (Rochelle et al. 2009) they can only be used in certain situations, such as shallower sediments under cold oceans bed and under extensive areas of icy hydrate formation, where it's possible that there is a lack of sufficient space for a CO₂ collecting plant.

The process of CO₂ hydrate storage mechanism involves buoyancy drives migration of liquid CO₂, which is capped by a developing impermeable CO₂ hydrate cap, (Figure 3 above). The CO₂ hydrate equilibrium zone is lowered by injecting liquid carbon dioxide into deep water or sub-permafrost sediments, (Rochelle et al. 2009). As more liquid CO₂ moves into the colder hydrate stable zone, a layer of impenetrable CO₂-hydrates builds inside the pore holes of the sedimentary reservoir rock. The US Department of Energy (DOE) on the other hand proposed a CO₂-EGR-based hydrate storage technology (enhanced gas recovery). CO₂ is injected into sediments that contain methane hydrates, releasing the methane from the hydrates and forming CO₂ hydrates in its place (Burnol et al. 2015). Because CO₂-EGR is still a novel idea, research into its effectiveness has been limited so far. According to Oldenburg (2003), one of the primary issues is the use of Methane which might in turn react with the injected CO₂ in an enhanced gas cycle, resulting in the gas resources being depleted.

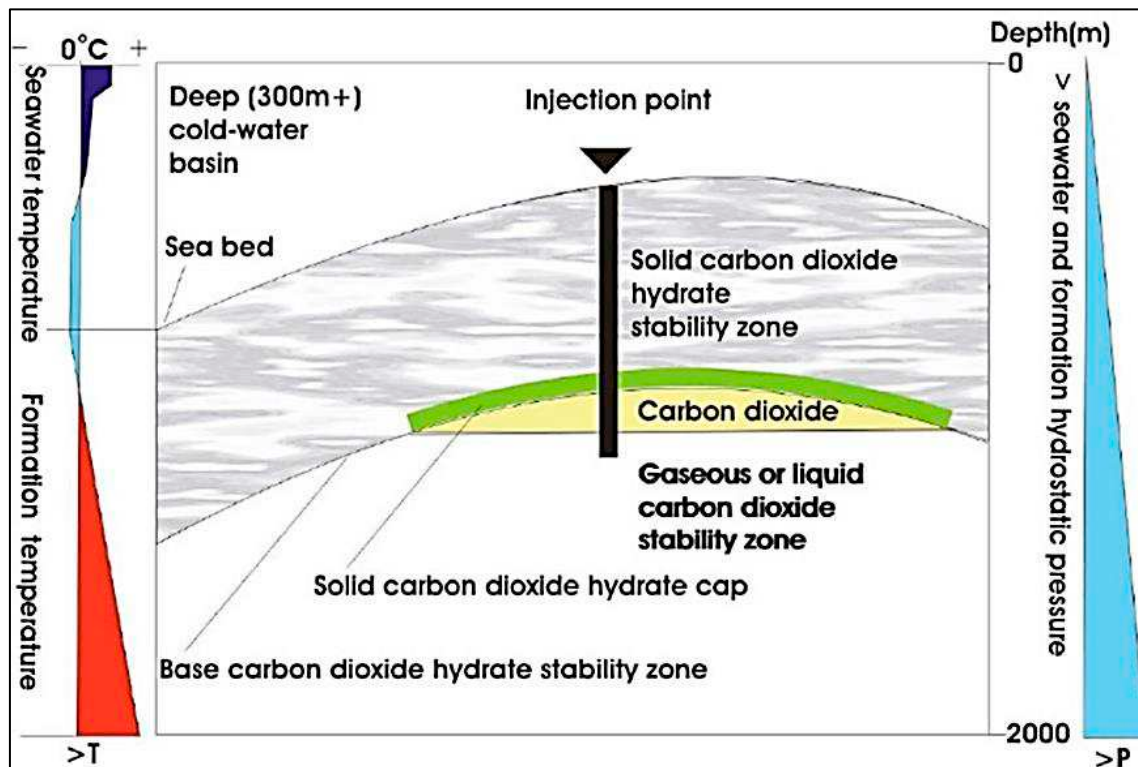


Figure 3. Illustration of Hydrate formation Diagram sequestration with its CO₂ Hydrate Seal, (Rochelle et al. 2009).

Presently, the technology required to store CO₂ in hydrates is not very advanced with most researches (Jemai et al. 2014), (Talaghat et al. 2009) focusing on theoretical modelling and lab-scale experiments Ghavipour et al. 2013), (Ruffine et al. 2010) and (Rehder et al. 2009). For this reason, there are still a number of challenges to be solved, especially with CO₂-EGR. However, local temperature and pressure fluctuations caused by drilling through hydrate-bearing sediments may destabilise the hydrate formation in its entirety (Khabibullin et al., 2011). How the CO₂-CH₄ hydrate exchange mechanism affects methane production, and how hydrate cap development may be shown as the major outstanding problems that need to be solved to improve the evaluation of hydrate storage viability.

2.7. Enhanced Geothermal Systems Based on CO₂

Previous studies (Garapati et al. 2015), (Pruess 2006), (Zhang and Song 2013) have emphasized that dense-phase CO₂, like water, has thermal characteristics that allow it to transfer large quantities of heat. However, it has better physical characteristics, such as substantially lower viscosity, more excellent compressibility, and expansibility. As a result, CO₂ may be utilised in the process of geothermal energy by extracting heat from the ground. CO₂ can efficiently reach the rock mass due to its low viscosity and may be considered as a medium for enhanced geothermal systems' operating fluid (Pruess 2006). Enhanced geothermal systems that use water as the heat transmission fluid suffer from the drawback of fluid loss. The inability to provide adequate water supplies is associated with financial difficulties because of the value placed on this resource. On the other hand, if upgraded geothermal systems (EGS) were to lose their reliance on CO₂, this would make underground geological storage of CO₂ possible, which might have further benefits.

It is essential for the effectiveness of CO₂-EGS storage that the rock mass loaded with CO₂ be separated from the surrounding rock mass, which is filled with water. These conditions are maintained in large part due to the formation of crystals of carbonate minerals at the interface between the CO₂-heavy centre of EGS with the brine-rich outside. Only countries having subsurface resources at economically feasible depths where the temperature is high enough would be able to use

this technology. Additionally, synergistic use of the subsurface may be more complicated and need more collaboration in heavily populated nations.

The technique is still in its early stages of technology readiness (TRL), with most research so far focused on theoretical modelling (Plaksina et al., 2016) and small-scale laboratory experiments. The main challenge to this method's development is the lack of clarity about the efficiency closing off the area surrounding the CO₂ source. To top it all off, nothing is known about the interactions between CO₂ and rocks at high temperatures. Understanding how CO₂ affects dissolution and precipitation, and how that affects changes in fracture permeability and EGS functioning, requires further study.

2.8. Carbonation of Mineral

Seifritz in 1990 was the first person to suggest the idea of CO₂ carbonation happening in the mineral as an alternative CO₂ sequestration method. The collected CO₂ is sequestered using this technique via the mineralisation process; in the presence of oxides or hydroxides of alkaline metals found in minerals, Carbonates are produced by the reaction of CO₂.

Incorporation of CO₂ into minerals may be accomplished in two ways: both in-and out-of-place. In-place technique includes injecting CO₂ into a geologic formation to produce carbonates. Meanwhile, the out-of-place process is carried out above the surface in a factory utilising rock that has been excavated earlier or rock that is indigenous to the area (Assima et al. 2014). In situ mineral carbonation is often discussed in high-magnesium, high-iron, and high-calcium silicate rocks like basalts and ophiolites (Ekpo Johnson et al. 2023). The in-situ mineral carbonation technique has significant benefits since it does not need substantial mining and just a few boreholes to complete the process. However, there may be significant unknowns, such as the absence of geological characteristics or the lack of knowledge on the possible cap-rock or seal.



Also, geochemical processes may decrease reactivity, porosity, and permeability, lining the resultant flow channels. There are both direct and indirect techniques that could be used to carbonate minerals outside of their natural environments. The direct gas-based technique comprises the interaction of gaseous CO₂ with minerals to form carbonates, as previously shown (Bobicki et al. 2012) and (Lim et al. 2010). Gas-solid carbonation normally occurs at temperatures below 65°C, with rate of chemical reaction and the amount of space available in rocks being the key limiting variables (Calabrò et al. 2008). The direct aqueous-based process consists of a single stage, which entails CO₂ interacting with mineral deposits in the presence of water. This step takes place in the presence of water (Bobicki et al. 2012). Direct mineral carbonation has significant challenges in commercial deployment and development due to minerals and carbon dioxide being dissolved and forming a product layer dispersion (Olajire 2013); (Bobicki et al. 2012)). When looking at the feasibility of long-term mineral carbonation that allows for the underground sequestration of carbon dioxide, Matter and Kelemen in 2009 turned to natural analogues. According to their findings, sedimentary rocks that have magnesium and calcium elements in quite high concentrations tend to have a high rate of mineralization. Their results reveal that carbonate mineral precipitation may fill gaps already present, but that the tension caused by fast precipitation may also cause fracture and an increase in pore volume. The mining industry has a snowball impact on the environment because some mineral deposits that are rich in calcium and magnesium may also include asbestiform components as well as other pollutants that are harmful to human health (IPCC Special Report 2005).

Two of the most common alkali and alkaline-earth metal oxides, magnesium oxide (MgO) and calcium oxide (CaO), don't really develop as binary oxides in free existence. Magnesium oxide has the chemical formula MgO, while calcium oxide has the chemical formula CaO. Compounds based on silicon dioxide, such as serpentine, are typical examples of this kind of assemblage. (Cipolli et al. 2004) and (Bruni et al. 2002) conducted studies on the effects of carbon dioxide on serpentine that had been retrieved from the spring waters of Genova. Serpentinization modifies the complex interaction

of ultramafic rocks with meteoric fluids, according to the results of a geochemical study of serpentinite-derived high-pH fluids and reaction-path simulation for aquifer-scale sequestration (Cipolli et al. 2004). MgHCO_3 waters are formed when CO_2 reacts with the rock, whereas Na-HCO_3 and Ca-OH type fluids are synthesised by further interactions with the host rock in a strongly lowering closed loop. Prior to employing reaction path modelling to simulate the process of injecting CO_2 at elevated pressure into aquifers formation, the findings suggested that serpentinites might be exploited for CO_2 sequestration because of their ability to create carbonate minerals. It should be emphasised that this method was only successful in reducing aquifer porosity under the circumstances of a closed system. This indicates that such consequences have to be examined thoroughly in both field and laboratory research.

Bruni and team in 2002 conducted research on the spring waters of the Genova area employing irreversible water-rock mass transfer. As a result of their investigation, they found some non-aligned Mg-HCO_3 fluids with several higher-pH Ca-OH fluids connected with serpentinites. They investigated if CO_2 sequestration is possible in the near and far future by dissolving serpentinite and then precipitating calcite. This was done in order to find out how effective this method might be. They determined that the interaction of these meteoric waters results in a gradual evolution in the chemistry of the aqueous phase. This development starts out with a magnesium-rich, low-salinity SO_4Cl facies and then moves on to intermediates facies made up of a more developed Ca-OH and Mg-HCO_3 compounds. In order to arrive at this result, scientists examined dissolved N_2 and Ar in addition to water's stable isotopes. Higher alkalinity of Calcium Oxide solvent can capture CO_2 and transform it into a deposits of Calcite formation or solute, this methodology might be used to sequester anthropogenic CO_2 .

On the downside, mineral carbonation might cause issues for both humans and the environment. Mineral carbonation processes have the potential to change the topography of an area in two different ways: via large-scale mining activities and, later on, through the disposal of reacted minerals. In addition, asbestiform phases and other potentially harmful pollutants may be present in some calcium- and magnesium-rich mineral formations (IPCC Special Report 2005).

Accordingly, future research should concentrate on:

- a. The potential for less terrain change
- b. Mineral carbonation in terms of mineral and CO_2 dissolution.
- c. Material stratum diffusion
- d. Managing mineral impurities throughout the sequestration process

2.9. CO_2 Sequestration in Ocean Floor Sediments

Intentionally injecting CO_2 into deep ocean floor is another option for anthropogenic CO_2 sequestration (IPCC,2018). The oceans cover around 70% of the planet. In the industrial era, they sucked up over a third of all man-made CO_2 emissions from the atmosphere and had an average depth of 3.8 km (Adams et al., 2008) and (Tanhua et al. 2013). Mathematical simulations have indicated that injected CO_2 may linger in the water for hundreds of years. This cold (1°C) and profound (4 to 5km) water flow slowly and may stay isolated from the atmosphere for millennia.

Direct CO_2 dissolution into seawater is the principal technique used in ocean storage. The first involves releasing CO_2 directly into the ocean floor, where it will form droplet plumes that will rise into the air. As an alternate method, liquid CO_2 is injected into a column, where it has the potential to interact with saltwater at a pace that is under control, therefore producing hydrate (Adams et al. 2008). Due to the fact that there is a potential for localised acidification of water from the sea in the vicinity of CO_2 injection location, the storage of CO_2 in the ocean floor is viewed with scepticism by a number of experts. This would have a deleterious effect on the benthic organisms. This is according to a series of recent studies published by Jacobson in 2009 and (Hofmann et al., 2010). Furthermore, it is unclear if international laws will permit CO_2 storage in the ocean as a development project. The London Convention for the Protection of the Marine Environment from Pollution by Dumping of Wastes and Other Matter into the Sea signed in 1996 put an end to the practise of discharging wastes from industrial processes into the ocean (Anon 2012a, Anon 2012b). Therefore, it is prohibited to

dump CO₂ into the ocean if it is considered an industrial waste. Although CO₂ was added to the "reverse list" in the London Protocol modification that allowed for the storage of CO₂ beneath the seabed in 2006, there is still no agreement on whether or not CO₂ should be classified industrial waste. "CO₂ may only be stored in compliance with an authorisation or permit given by the Party's competent authority," as stated in the North-East Atlantic Convention with the Interest of Preserving the Quality of the Marine Environment (Anon 2017), (ZeroCO₂ 2015). Therefore, it is necessary to evaluate the ambiguity surrounding ocean sequestration and its effects on the ecosystem, and to provide solutions to possible problems that may arise.

Oceanic sequestration efficiency may be evaluated based on a number of criteria, the most important of which are injection depth, residence time, and CO₂ concentration allocation. (Xu et al. 1999) constructed a regional ocean general circulation model that assumed there was no air-to-sea CO₂ exchange and investigated the prospect for CO₂ sequestration in the North Pacific by using a wide range of sub-grid mesoscale mixing parameters. According to their findings, storage depth is a crucial factor in sequestering CO₂ and limiting its emissions back into the atmosphere. It was discovered that a depth of injection of more than 1,000 metres is necessary so as to slowly release CO₂ into the water over the period of very few 100 years.

Following fifty years of constant injection of CO₂, more than ten percent of the dissolved CO₂ would be released back into the environment. This leakage should be considered as a major concern. Adcroft et al. in 2004 used an ocean circulation model to assess the storage efficiency of impulse injections based on mean residence time. CO₂ sequestration was more successful in the North Atlantic over hundreds of years, whereas it was more successful in the Pacific basin over shorter time periods. In spite of the fact that the magnitudes that were tested were low and that the impact of air-sea CO₂ circulation were ignored, the relevance of this effect over large borders is still a concern and calls for more research.

In order to assess the efficacy of a potential sequestration location, the variation in CO₂ concentration after injection might be considered. A place where CO₂ is adequately diluted while having little environmental impact is preferable. However, by simulating CO₂ injection into a number a model of the ocean's main circulation at several sites around Japan, the spatial variability of CO₂ content with respect to injection rate and eddy activity distribution has been studied (Masuda et al., 2008) These researchers used an ocean general circulation model to perform their research. Specifically, the data indicated that the highest CO₂ concentration may vary by a factor of 10 across places, where the principal driver of this variation is the regionalization of turbulent events. Additionally, it has been established that keeping injection rates below 20Mt/a would have little long-term impact on biota.

In order to advance the discussions surrounding the evaluation of oceanic sequestration, previous study has shown that a number of improvements and unknowns need to be investigated and resolved in future studies. One way to boost storage efficiency is by updating the present numerical model to account for CO₂ exchange between the atmosphere and the ocean, and second, reducing the number of assumptions underlying the model, further investigating the determination of storage efficiency.

3. Conclusion

This paper provides a comprehensive review on the current advancements in CO₂ sequestration with special interest on deep aquifer CO₂ storage. This highlights significant steps that has been covered so far, as well as obstacles that still need to be address for geological subsurface CO₂ sequestration, and approaches adopted in calculating CO₂ storage capacity.

Even though carbon dioxide sequestration by storage in the ocean and storage through the process of carbonation has been established, CSS remains the most viable option practical alternative because of financial concerns, vast geographical dispersal, and environmental difficulties. This is the case because it has been proven that carbon dioxide can be sequestered.

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Abbreviations

GHG, IEA, NASA, GCCSI, IPCC, CO₂-EOR, IEAGHG, DOE.

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