



CLIMATE CHANGE: MITIGATION STRATEGY BY VARIOUS CO₂ SEQUESTRATION METHODS

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ABSTRACT

The ever-growing energy demands worldwide have been satisfied through the use of fossil fuels. The repercussion of this has been the increase in carbon dioxide concentration in the atmosphere. Given the adverse effect of high levels of CO₂ in the atmosphere, there is a recognized need for strategies to mitigate the effects. The approach to research in this area includes studies which investigate the capture and safe, permanent disposal of CO₂. In the present study, various technological options have been suggested for the purposes of safe storage of CO₂—for example, geological (e.g., depleted oil and gas reservoirs, oceans, and aquifers), biological and mineral storage.

I INTRODUCTION

The entire world is grappling with the increase of carbon dioxide in the atmosphere and its adverse environmental impact. CO₂ is the largest contributor by volume to the purported greenhouse gas effect; Methane (CH₄), Nitrous Oxide (N₂O) and other halocarbons being the other contributors. It was observed that the atmospheric CO₂ concentration levels started rising significantly shortly after the industrial revolution and has continued to do so till date. The atmospheric CO₂ concentration had increased significantly from 280 ppm in Pre-Industrial era to 385 ppm in 2008 (Modern era). Notably, it is observed that the atmospheric CO₂ concentration shows a steep growth rate of 2 ppm on an average since the turn of the millennium (Brierley and Kingsford 2009). High atmospheric CO₂ concentration causes global climate change leading to devastating effects on ecosystems and cause calamities such as drought, floods, and cyclones. Moreover, various organisms are under the threat of extinction due to the changes caused in the ecosystem (Marini 2007). It is observed that atmospheric CO₂ concentration and mean global temperature are directly proportional. Though this does not necessarily prove a direct cause–effect relationship, it still holds significance as it shows that the rise in atmospheric CO₂ concentration is a contributor to Global Warming. Thus, it is required to devise new strategies to meet energy demands with techniques that have lower emissions or none (IPCC 2005). There are three notable strategies for reducing CO₂ emissions namely: by using energy efficient technologies with decreased fossil fuel consumption, by using renewable energy resources not derived from fossil fuels such as solar, wind, biomass



and nuclear and by using Carbon Capture and Storage (CCS) technology. Though the first two solutions have gained traction over the last few years to reduce CO₂ emissions, there is still a conceivable need to manage the CO₂ emissions that take place. Therein lies the need for CCS technology. In CCS technology, CO₂ is separated from the flue gas of a static CO₂ source such as a power plant utilizing fossil fuels and subsequently stored for long-term isolated from the atmosphere (IPCC 2005). The process of CCS occurs in three stages: capture, transport, and storage. The CO₂ is collected from a static emitter, usually a power plant, and is then routed to a storage site through pipes.

It is found that there are four viable storage sites (also known as carbon sinks) with different characteristics with respect to their limitations, longevity, and costs involved. These alternatives are classified as mineral, biological, geological and ocean storage methods. The atmosphere holds roughly 60% of the carbon emissions, the other 40% being retained in “carbon sinks”, such as vegetation, bodies of water and rocks. The world's biggest carbon sink are carbonate rocks which is a form of mineral storage method (Liu and Zhao 2000). The captured CO₂ needs to be stored permanently in order to avoid its re-emission back into the atmosphere. It is also found that mineral storage has the highest CO₂ storage capacity and hence can effectively sequester all existing CO₂ emissions as shown in Table 1. Another distinguishing characteristic of mineral storage is that it is safer than other forms of sequestration such as biological or ocean storage methods, which are plagued by environmental concerns (Lackner 2002; Huijgen and Comans 2003; Sipilä et al. 2008; Hitch et al. 2010; Sanna et al. 2014).

Table 1:Estimated potential of CO₂ storage and utilization options(Huijgen and Comans 2003)

Option	Estimated global capacity [Gt of CO ₂]
Mineral CO ₂ sequestration	Very large (more than the total release of oxidation of global fossil fuel reservoirs)
Ocean disposal	>1,000
Saline aquifers	>100
Depleted gas reservoirs	>140
Depleted oil reservoirs	>40
Improved forestry and reforestation	50-100
Enhanced oil recovery	65
Bio fixation	1.35
Chemicals	0.09

II METHOD OF CO₂ SEQUESTRATION

CO₂ sequestration through geological, biological, ocean and mineral storage methods are described below.

2.1. Geological Sequestration

Geological sequestration is an underground storage method which is currently implemented for CO₂ sequestration. The possible sites for geological storage are oil and gas reservoirs, deep coal seams, saline



aquifers and salt caverns.

2.1.1. Oil and Gas Reservoirs

The storage of CO₂ inside oil and gas reservoirs is found to be the most appealing geological sequestration method in recent times due to the highest CCS capacity among the geological sequestration methods. It still suffers from the pitfalls associated with geological sequestration such as high leakage rate and inadequate capacity compared to other carbon sequestration methods (Park 2005).

Oil and gas reservoirs are further classified into active and depleted reservoirs. Both types are viable for the sequestration process. There are three factors that affect the CCS efficiency in these sites, namely: presence of underground water, the distance between the storage site and the emission source and leakage rate. Wet reservoirs where a large volume of water is present offer little accommodation for CO₂ storage in contrast to dry reservoirs. Gas fields offer maximum storage of CO₂, almost equal to that of the original gas quantity due to negligible presence of water (Holloway 2005). The insertion of CO₂ into the oil and gas reservoir increases pressure on the site which helps boost the potential extraction quantity of oil and/or gas through secondary recovery. It is estimated that, during this process, when CO₂ is injected to recover oil and gas, extracted volume can be increased by upto 15% in gas recovery and upto 50% in oil recovery in active reservoirs (IEA, 2004). Enhanced Gas Recovery (EGR) and Enhanced Oil Recovery (EOR) methods thus provide a more economical solution for CO₂ insertion (IEA 2004). While these options appear to be frugal and offset the costs incurred for CCS, it is sensitive to location (i.e.) the distance between the storage site and the emission source affects the costs substantially (IEA 2004). It should be ensured that the sum of insertion and transportation expenses must not exceed the secondary recovery value threshold to keep it viable (Ragnheidardottir 2010). Another issue to reckon with is the longevity of these storage sites due to the possible leakage caused by impermanence of crust and other unforeseen conditions (Levi 2005). This requires long-term monitoring to manage potential leakage given its associated health and safety risks.

2.1.2. Deep Coal Seams

Deep coal seams also provide a viable host for CO₂ sequestration with high permanence. There are fractures within coal seams commonly referred to as “cleats”. These pore spaces can host CO₂ permanently without leakage. The storage capacity will vary by region and so a case by case analysis is always important since there is no real standardization analysis available (IPCC 2005). The recovery of coal-bed methane (CBM) is dependent on the pressure and temperature in exhausted coal seams. Both pressure and temperature are enhanced during CO₂ injection (Voormeij and Simandl 2004).

2.1.3. Deep Saline Aquifers

Deep saline aquifers are another geological storage option that offer high storage capacity. Globally, they are



found in most of the sediment basins. Saline aquifers are reservoirs of water with high salt concentration that is not fit for human consumption (Voormeij and Simandl 2004). Prior to the development of CO₂ sequestration, saline aquifers were used as storage sites for other forms of hazardous waste. Aquifers, when used as carbon sinks present only a small portion (approx. 2%) of their available volume for the deposit of CO₂. It also suffers from risk of high leakage rate given the likely occurrence of cap fractures (Voormeij and Simandl 2004). CO₂ sequestration in the aquifer is affected by buoyancy, surface area of undissolved CO₂ and the differences in density and viscosity between the injected CO₂ and the aquifer water. Buoyancy effect causes CO₂ inserted into an aquifer water to rise and then gradually disperse into a layer underneath the cap of the aquifer (Gale 2004). The most pronounced process in the initial stages of the reaction is the dissolution of CO₂ into the aquifer water and this rate of dissolution is dictated by the surface area of undissolved CO₂ in contact with the aquifer water (Gunter et al. 1997). Since CO₂ separates and moves upward at a faster rate when density and viscosity differences between CO₂ and the aquifer water is higher, it is necessary to insert CO₂ under high pressure to ensure high CO₂ density and thus increase CO₂ solubility in the aquifer water (Voormeij and Simandl 2004).

2.1.4. Salt Caverns

Salt caverns are another geological storage option that offer high permanence. They are defined as the massive cavities that remain after extraction of salt by injecting water in an underground salt bed and removing salt in the form of brine (Voormeij and Simandl 2004). They offer spaces as large as $5 \times 10^5 \text{ m}^3$ in volume available for CO₂ storage (Bachu 2000). Given the impermeability of salt layers, the caps of these spaces would be potent barriers against leakage (Levi 2005). However, this storage site has two major problems: environmental concerns with respect to the disposal of brine and high costs (Voormeij and Simandl 2004). Hence, this method is not widely viewed as a viable option.

2.2. Biological Sequestration

Trees and other vegetation host CO₂ during photosynthesis. During photosynthesis, plants absorb CO₂ along with water and convert it into low-carbon compounds, for e.g., cellulose or starch. Biological sequestration by photosynthesis whether in soil or biomass has a sequestration capacity of approximately 100 Gt of carbon per year making it a viable option (Park 2005). Another biological option is marine biological sequestration where CO₂ is sequestered in marine plants. The associated costs of biological sequestration are usually very low; for example, forest planting in developing nations may be as low as 3 to 10 USD per ton of CO₂ captured (Paustian et al. 1998). Biological sequestration poses the risk of less carbon efficient natural ecosystems being supplanted by monocultures for the purpose of CCS creating an imbalance in the ecosystem. Marine biological sequestration also has other disadvantages such as insufficient CCS capacity and disruption of the marine food chain.

2.3. Ocean Sequestration



Ocean sequestration commonly referred to as deep ocean sequestration is the largest CO₂ host method having CCS potential greater than the combined CCS potential of geological and mineral storage methods. A significant fraction of CO₂ is naturally sequestered by the ocean without any effort by exchange of CO₂ between atmosphere and ocean water until chemical equilibrium is established. The equilibrium concentration of CO₂ between the atmosphere and the ocean is approximately 1:4. Ocean sequestration however is not permanent as the dissolution is directly proportional to depth. Therefore, high sequestration permanence and high sequestration capacity can be achieved simultaneously through deep insertion at depths below 1500 m. Oceans are estimated to be capable of hosting CO₂ for a maximum of 500 years post which the CO₂ is re-emitted back to the atmosphere (Voormeij and Simandl 2004). Currently, it cannot be determined precisely when that occurs. Until a means of quantifying that time period is created, ocean sequestration remains questionable (Levi 2005). Ocean sequestration also poses environmental concerns such as climate change and marine chemical changes. Also leakages can occur by sudden expulsion of stored CO₂ during volcanic activity and mantle plumes within the ocean (Park 2005). CO₂ leakage can also occur due to its lower density compared to ocean water which causes droplets of CO₂ to move upward until dissolution occurs and subsequently this CO₂-saturated solution will fan out into the surrounding ocean water. The leakage can be reduced if CO₂ sequestration is done at greater depths as discussed earlier but advanced technology is required for deep insertion which increases the costs (Voormeij and Simandl 2004).

2.3.1. Storing CO₂ as Clathrates

Another method of ocean sequestration is to spawn lakes of CO₂ on the ocean floor at depths below 3000 m. Depths of this magnitude create high water pressure and provide low temperature due to limited supply of sunlight which converts CO₂ into its liquid state that has a higher density than ocean water. Reaction between CO₂ and the ocean water will create a clathrate, which is a cage matrix comprised of roughly six H₂O molecules for every CO₂ molecule (Sloan 2003). Pure CO₂-hydrate has a higher density than ocean water and will produce a falling plume which will rest on the ocean floor (Brewer et al. 2000). This technique would cause the agglomeration of sequestered CO₂ in the deep sea trenches (Voormeij and Simandl 2004). However, CO₂-hydrates are unstable and will dissolve when CO₂ concentration levels in ocean water return to normal levels subsequently leading to CO₂ leakage. This poses environmental risks causing changes to the ocean chemistry eventually causing adverse impacts on the marine ecosystem.

2.4. Mineral sequestration

Mineral sequestration is another viable carbon sequestration method which offers high-capacity storage (>10,000 Gtof CO₂), which means the worldwide supply of minerals can likely sequester all future emissions (Sanna et al. 2014). The interest in mineral sequestration is most pronounced in regions where underground sequestration is impossible or decidedly unfeasible (Sipilä et al. 2008). There are two significant advantages mineral sequestration has in comparison to other options (e.g., geological): the safety and permanency of CO₂ sequestration in the thermodynamically stable product of carbonation and the sheer

abundance of viable feedstock. This post-sequestration monitoring is unnecessary(Liu and Zhao 2000).

Table 2: Feedstock for mineral carbonation

Feedstock	Examples
Natural minerals	Wollastonite, olivine, serpentine, feldspar, basalt, brucite, pyroxene, forsterite, dunite
Industrial wastes	Steel slag, cement waste, fly ash, MSWI ash, paper mill waste, oil shale ash, mine tailing

The most abundant minerals utilized in carbonation reactions are those rich in calcium and magnesium such as olivine and wollastonite(Huijgen and Comans 2003). High concentrations of magnesium and calcium-based compounds in many industrial by-products and residues are also candidates for sequestration—for example, iron and steel slags, different types of process ashes, and cement-based waste materials as listed in Table 2(Eloneva et al. 2009). Though the total amount of residues and by-products is smaller than that of naturally-sourced materials, they are easy to acquire, continuously spawned, and are often more conducive to reaction than natural materials. Also, the products (e.g., pure CaCO_3) of the process may have industrial applications(Motz and Geiseler 2001; Teir et al. 2007).

2.4.1.Mineral carbonation route

Various process routes have been studied in the literature with the majority of these routes can be classified into two categories: direct carbonation or indirect carbonation routes. Direct carbonation route utilizes a single step carbonation process in which both the dissolution of minerals and carbonation reaction occurs in a single reactor.A problem with this approach is that its reaction rates under atmospheric conditions occur at a speed not considered viable for industry; therefore, research has focused on the acceleration of this process(O'Connor et al. 2002). Indirect carbonation utilizes several additive chemicals such as HCl, H_2SO_4 and HNO_3 to accelerate the carbonation process(Baciocchi et al. 2010; Bao et al. 2010). Indirect carbonation route occurs in two steps. In the first step, extraction of reactive minerals occurred at low pH and then carbonation at a higher pH in a separate reactor. A list of different carbonation routes is given in Table 3.

Table 3: Different carbon sequestration routes

Carbonation method	Route
Direct carbonation	Single step gas-solid carbonation
	Single step aqueous carbonation
	-Without additive
	-Additive enhanced
	Molten salt



Indirect carbonation	Two step gas-solid carbonation
	HNO ₃ acid
	CH ₃ COOH acid
	HCl acid
	NH ₄ -salt extraction
	Precipitated CaCO ₃
	pH swing
	Three steps- caustic soda
	Molten salt
	Brine solution
	Duel alkali

The process can also be substantially improved by reducing the size of the mineral. Thermal or mechanical activation and optimization of the chemical process also dramatically enhances the rate of reaction(Goff and Lackner 1998). In recent years, diverse process methods and optimization techniques developed in lab scale experiments have been shown to substantially improve conversion rates(Sanna et al. 2014). Carbonated products have applications in construction and mine reclamation(Motz and Geiseler 2001). Currently, given a lack of substantial data, it is not possible to determine whether an economically and energetically frugal method is feasible. Though mineral carbonation is a distant option in contrast to other methods, its advantages warrant continued research. Major concerns that need to be addressed prior to industrial deployment of mineral sequestration are the energy consumed by the method, the rates of reaction, and the environmental effect of the method.

III COST OF SEQUESTRATION

Table 4: Cost of sequestration(IPCC 2005)

Method for CO ₂ sequestration	Cost \$/t of CO ₂
Geological ^a	0.5-8.0
Ocean	6-31
Biological ^b	3-10
Mineral Carbonation	50-100

^aExtra cost for monitoring ranging from \$0.1 to 0.3/t of CO₂

^b(Paustian et al. 1998)

CO₂ sequestration through geological method offers best carbonation method for a large amount of CO₂ storage due to their low cost. However, due to higher cost, mineral carbonation offers a better solution for small and medium emissions, meaning those below 2.5 Mt CO₂, which constitutes roughly 10 to 15% of all CO₂ emissions(Sanna et al. 2014). The expenses associated with the mineral sequestration method are higher than



those of others method, but those costs may be mitigated by the possible industrial applications of its by-product (Voormeij and Simandl 2004).

Table 5: Comparison of CO₂ sequestration methods

Sequestration methods	Advantages	Disadvantages
Geological	<ul style="list-style-type: none"> • Low cost 	<ul style="list-style-type: none"> • Less permanency • Monitoring for geological lifetime
Mineral	<ul style="list-style-type: none"> • High capacity • Environmentally safe • Permanent • No monitoring • Utilization of industrial waste 	<ul style="list-style-type: none"> • High cost • Slow reaction kinetics • Energy intensive • Pre-treatment of feedstock required to increase carbonation rate • Poor recovery of additive chemicals • Mining of feedstock create environmental issues • Disposal or use of the process product if implemented in large scale

IV CONCLUSION

This study discussed various aspect of CO₂ sequestration. Four types of sequestration methods have been described in details. These methods can be used to sequester CO₂ and mitigate its effect on global warming. However, adoption of any method depends on various parameters such as geological location, the amount of sequestration required, and process cost.

REFERENCES

- [1.] Bachu S (2000) Sequestration of CO₂ in geological media: Criteria and approach for site selection in response to climate change. *Energy Convers Manag* 41:953–970. doi: 10.1016/S0196-8904(99)00149-1
- [2.] Baciocchi R, Costa G, Latégano E, et al (2010) Accelerated carbonation of different size fractions of bottom ash from RDF incineration. *Waste Manag* 30:1310–1317. doi: 10.1016/j.wasman.2009.11.027
- [3.] Bao W, Li H, Yi Z (2010) Selective leaching of steelmaking slag for indirect CO₂ mineral sequestration. *Ind Eng Chem Res* 49:2055–2063. doi: 10.1021/ie801850s



- [4.] Brewer PG, Peltzer ET, Friederich G, et al (2000) Experiments on the ocean sequestration of fossil fuel CO₂: pH measurements and hydrate formation. *Mar Chem* 72:83–93. doi: 10.1016/S0304-4203(00)00074-8
- [5.] Brierley AS, Kingsford MJ (2009) Impacts of Climate Change on Marine Organisms and Ecosystems. *Curr Biol* 19:R602–R614. doi: 10.1016/j.cub.2009.05.046
- [6.] Eloneva S, Teir S, Revitzer H, et al (2009) Reduction of CO₂ Emissions from steel plants by using steelmaking slags for production of marketable calcium carbonate. *Steel Res Int* 80:415–421. doi: 10.2374/sri09sp028
- [7.] Gale J (2004) Geological storage of CO₂: What do we know, where are the gaps and what more needs to be done? *Energy* 29:1329–1338. doi: 10.1016/j.energy.2004.03.068
- [8.] Goff F, Lackner KS (1998) Carbon dioxide sequestering using uitramaf IC rocks. *Environ Geosci* 5:89–101. doi: 10.1046/j.1526-0984.1998.08014.x
- [9.] Gunter WD, Wiwchar B, Perkins EH (1997) Aquifer disposal of CO₂-rich Greenhouse Gases: Extension of the time scale of experiment for CO₂-sequestering reactions by geochemical modelling. *Mineral Petrol* 59:121–140. doi: 10.1007/BF01163065
- [10.] Hitch M, Ballantyne SM, Hindle SR (2010) Revaluing mine waste rock for carbon capture and storage. *Int J Mining, Reclam Environ* 24:64–79. doi: 10.1080/17480930902843102
- [11.] Holloway S (2005) Underground sequestration of carbon dioxide - A viable greenhouse gas mitigation option. *Energy* 30:2318–2333. doi: 10.1016/j.energy.2003.10.023
- [12.] Huijgen WJJ, Comans RNJ (2003) Carbon dioxide sequestration by mineral carbonation, literature review. *Energy research Centre of the Netherlands (ECN)*
- [13.] IEA (2004) *Energy Technology Analysis: Prospects for CO₂ Capture and Storage*. 249. doi: 10.1016/B978-1-85617-710-8.00010-8
- [14.] IPCC (2005) *IPCC Special Report on Carbon Dioxide Capture and Storage*.
- [15.] Lackner KS (2002) Carbonate Chemistry for Sequestering Fossil Carbon. *Annu Rev Energy Environ* 27:193–232. doi: 10.1146/annurev.energy.27.122001.083433
- [16.] Levi RD (2005) Belvidere Asbestos Mine: Site Suitability for CO₂ Sequestration Through Mineral.
- [17.] Liu Z, Zhao J (2000) Contribution of carbonate rock weathering to the atmospheric CO₂ sink. *Environ Geol* 39:1053–1058.
- [18.] Marini L (2007) Geological Sequestration of Carbon Dioxide - Thermodynamics, Kinetics, and Reaction Path Modeling. *Dev Geochemistry* 11:27–51. doi: 10.1016/S0921-3198(06)80023-2
- [19.] Motz H, Geiseler J (2001) Products of steel slags an opportunity to save natural resources. *Waste Manag* 21:285–293. doi: 10.1016/S0956-053X(00)00102-1
- [20.] O'Connor WK, Dahlin DC, Rush GE, et al (2002) Carbon dioxide sequestration by direct mineral carbonation: Process mineralogy of feed and products. *Miner Metall Process* 19:95–101.
- [21.] Park A-HA (2005) Carbon dioxide sequestration: chemical and physical activation f aqueous carbonation of Mg-bearing mineral and pH swing process. 176.



- [22.] Paustian K, Cole CV, Sauerbeck D, Sampson N (1998) CO₂ mitigation by agriculture: An overview. *Clim. Change* 40:135–162.
- [23.] Ragnheidardottir EV (2010) Costs , Profitability and Potential Gains of the CarbFix Program.
- [24.] Sanna A, Uibu M, Caramanna G, et al (2014) A review of mineral carbonation technologies to sequester CO₂. *Chem Soc Rev* 43:8049–80. doi: 10.1039/c4cs00035h
- [25.] Sipilä J, Teir S, Zevenhoven R (2008) Carbon dioxide sequestration by mineral carbonation Literature review update 2005–2007.
- [26.] Sloan ED (2003) Fundamental principles and applications of natural gas hydrates. *Nature* 426:353. doi: 10.1038/nature02135
- [27.] Teir S, Eloneva S, Fogelholm CJ, Zevenhoven R (2007) Dissolution of steelmaking slags in acetic acid for precipitated calcium carbonate production. *Energy* 32:528–539. doi: 10.1016/j.energy.2006.06.023
- [28.] Voormeij DA, Simandl GJ (2004) Geological, ocean, and mineral CO₂ sequestration options: A technical review. *Geosci Canada* 31:11–22. doi: 10.12789/gsc.v31i1.2740