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Carbon Capture and Storage: A Review of Mineral Storage of CO_2 in Greece

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Abstract: As the demand for the reduction of global emissions of carbon dioxide (CO_2) increases, the need for anthropogenic CO_2 emission reductions becomes urgent. One promising technology to this end, is carbon capture and storage (CCS). This paper aims to provide the current state-of-the-art of CO_2 capure, transport, and storage and focuses on mineral carbonation, a novel method for safe and permanent CO_2 sequestration which is based on the reaction of CO_2 with calcium or magnesium oxides or hydroxides to form stable carbonate materials. Current commercial scale projects of CCS around Europe are outlined, demonstrating that only three of them are in operation, and twenty-one of them are in pilot phase, including the only one case of mineral carbonation in Europe the case of CarbFix in Iceland. This paper considers the necessity of CO_2 sequestration in Greece as emissions of about 64.6 million tons of CO_2 annually, originate from the lignite fired power plants. A real case study concerning the mineral storage of CO_2 in Greece has been conducted, demonstrating the applicability of several geological forms around Greece for mineral carbonation. The study indicates that Mount Pindos ophiolite and Vourinos ophiolite complex could be a promising means of CO_2 sequestration with mineral carbonation. Further studies are needed in order to confirm this aspect.

Keywords: carbon capture and storage; mineral carbonation; CO_2 sequestration; Greek power plants

1. Introduction

Nowadays, there is an increasing demand for energy, which has resulted in an increase in the use of fuels, particularly conventional fossil fuels (coal, oil and natural gas). Despite the fact that fossil fuels have been the key energy source since the industrial revolution, they have simultaneously caused a serious threat to the environment through their combustion, thus emitting high amounts of CO_2 into the atmosphere, which is a major anthropogenic greenhouse gas. It is clear that human activities influence the climate system [1]. In 2016, the average concentration of CO_2 (403 ppm) was 40% higher than in the mid800s [2], and it has been estimated that the CO_2 concentration has increased about 2 ppm/year in the last ten years [2]. In light of the global commitment achieved in Paris 2015, the rise in global temperature should be kept below 2 °C compared to pre-industrial levels and the temperature increase should be limited to no more than 1.5 °C (UN Paris Agreement 2015) [3]. According to the international energy agency (IEA) [2], reaching the goal set by the Paris Agreement requires the storage of at least 1 gigaton of CO_2 annually by 2030. One critical technology that could help in the fulfillment of the above goals is CCS. The objective of CCS is to capture and store CO_2 in several ways [4]. CCS uses the existing processes and technologies available in the oil and gas industries to capture the CO_2 and store it deep below the surface in appropriate geological formations for permanent storage [4–6].

The aims of this paper are to present several CO_2 capture, transportation and storage strategies, according to the literature, and also discuss the CCS technologies around Europe. Focusing on the third part of the CCS chain (storage), it is concluded that mineral carbonation could be a promising CO_2 storage technique. Taking into account that lignite combustion is the main industrial method of electricity production in Greece, it emits high amounts of CO_2 and there are few studies about the establishment of CCS technologies in Greece, an investigation into the potential CO_2 storage sites for mineral carbonation was conducted. The geological formations that are found to be more suitable for binding CO_2 with mineral carbonation according to the literature are basalt and ophiolite rocks [5,7–10]. Based on the literature, the appropriate geological formations in Greece that could serve as CO_2 storage sites for mineral carbonation were investigated. Focusing on the Greek Power Plant area, it is recommended that mineral carbonation in the sites of Vourinos and Pindos under appropriate conditions could be a potentially safe and permanent way of sequestrating CO_2. This study, offers a choice of reducing the greenhouse gas emissions from fossil energy use in a way that can facilitate future development goals. It does this by avoiding the elimination of fossil fuels use and thus ensuring the minimal disruption of financial activities and jobs.

2. Literature Review

2.1. CO_2 Capture Technology

There are three technological routes for CO_2 capture from power plants: Pre-combustion capture, where fuels are converted to H_2 and CO_2 and the CO_2 produced is separated before combustion; post-combustion capture where CO_2 is separated from the flue gas, which is produced by fuel combustion; and oxy-fuel, where pure oxygen is used instead of air during combustion, leading to a flue gas stream of nearly pure CO_2. However, the application of this technology may reduce the efficiency of the plant by 14% and increase the cost of electricity by 30–70%) [11]. The post combustion capture is of particular interest because it is a possible near-term CO_2 capture technology that can be used to existing power plant [6]. As a result, this paper focuses mainly on post combustion technologies.

Chemical absorption is one type of CO_2 capture technology. The classic CO_2 absorbent is aqueous monoethanolamine (MEA), especially for CO_2 separation in electricity generation [4,12,13]. The first full-scale commercial post-combustion carbon capture and sequestration project was operated in a coal fired power plant in Estevan, Saskatchewan, Canada that used an amine-based process reducing CO_2 emissions. New absorbents [4] have been studied for this purpose, such as single amine absorbents, amine blends, multi face absorbents, e.g., the formulation of aqueous piperazine (PZ) and 2-amino-2-methyl-1-propanol (AMP), econamine FG+, KS-1 and Cansolv. Due to the fact that this kind of absorbents shows some disadvantages as high cost, low capture capacity and high energy consumption [14,15], it was investigated the potassium carbonate K_2CO_3 as an alternative to amines and found to be a promising absorbent with many advantages [15,16].

Adsorption is another technology used for CO_2 capture. The use of the adsorption process in electric power plants indicated that this technique could be used for power plants [17,18]. Some classical adsorbents are carbons, aluminas, zeolites, silicas, metal organic frameworks, hydrotalcites, poliymers etc. More details about adsorption in CO_2 capture technologies and their development are indicated by Bui et al. [4].

Another process, that is relatively new, was proposed by Shimizu et al. [19] for CO_2 removal from the flue gas released from air-blown combustion systems. The calcium looping process separates CO_2 using the reaction $CaO + CO_2 \rightarrow CaCO_3$ and the regeneration of CaO using O_2 combustion. The key advantages of this technique are of interest: A large amount of high recoverable heat (600−900 °C); the possible increase in the power plant energy penalty (40−60%); no flue gas cooling and pretreatment (SOx); and finally, it has low emissions and an affordable price [20]. A review of the calcium looping technology and its progress has been presented by Bui et al. [4].

Another technology for capturing CO_2 from coal fired power plants is chemical looping [21,22], which is in its early stage of development, has the potential of a very low efficiency penalty and low CO_2 avoidance cost [23]. Details about the progress of this technology can be found in Bui et al. [4]. Membrane-based processes can be used in pre-combustion, oxy-combustion and post-combustion, and are suitable for coal fired power plants. The development of this technology is reported by Bui et al. [4].

Ionic liquids (ILs) technology has attracted attention, due to the energy and cost-efficient separation of CO_2 from post-combustion flue gas [24].

There are also technologies, such as BioEnergy, with CCS (BECCS) and direct air capture, and sequestration (DAC), which allow for the net CO_2 removal from the atmosphere, and are referred to as negative emissions technologies. The technology of BECCS depends on the assumption that biomass sequesters CO_2 from the atmosphere as it grows and hence results in a net removal of CO_2 from the atmosphere [4,25]. However, this approach has serious problems such as the need for arable land, which it would be preferential to be used for food production and not for biomass [4]. The increase in electricity cost, and the decrease in energy security is another serious problem [25].

The DAC process depends on the capture which takes place directly through the atmosphere via absorption or adsorption processes. There is a DAC plant in Hilwil, Switzerland that filters CO_2 from the atmosphere and supplies 900 tons of it annually to a nearby greenhouse that acts as an atmospheric fertilizer (Grand opening of Climeworks commercial DAC plant, Gasword, 2017). Similarly, in Vancouver, BC, Canada (Carbon Engineering) DAC technology can be scaled up to capture one million tons of CO_2 per year. DAC is a promising approach; however, it cannot replace the conventional CCS systems because the CO_2 concentration in air is 100 to 300 times lower than in the flue gas of gas or coal fired power plants. This results in a high cost of capturing CO_2 from the air than from point sources and hence constrains the use of DAC [26].

2.2. CO_2 Transportation

In the CCS process, after the CO_2 is captured and separated, the gas is transported to the storage site via a pipeline when it is in a dense phase or by trucks, rail, and ships when it is in a liquid phase. The efficacy of the methods depends on the distance of each point of storage. Ideally, CO_2 would be stored where it is captured. According to Zero emissions platform [27], for large distances >1500 km, transportation via ship is preferable because of the lower cost. Generally, the vast majority of transportation is expected to be via pipelines because they have a number of advantages [28], such as continuous transport from the source to the storage site, which is essential, especially for power plants, that operate continuously and is also a more economical way of transportation than other ways like ships [27,28]. However, there are also some difficulties. The amount of CO_2 that is transported should be in the dense phase, otherwise the system will have operational problems. For this purpose the appropriate temperature and pressure must be chosen so that the phase remains the same along the length of the pipeline [4,28]. Furthermore, the impurities in the CO_2 stream are of great importance and impact on the design and operation of the pipeline system [28]. Generally, it is considered that the cost of transporting CO_2 may be considerably reduced by using multiple diameter trunk lines that lower the operating costs and ensure at the same time that there is the right operating pressure throughout the whole pipeline [4,28,29]. CO_2 transportation via ships can be an effective cost solution for very long distances and for low quantities from small sources [30]. Details about the technology of CO_2 shipping can be found in Brownshort et al. [31].

2.3. CO_2 Storage

CO_2 storage is the last step in the CCS chain. The CCS process comprises of ocean storage, geological storage, and mineral carbonation [32]. Geological storage is considered to be the most viable option and includes depleted oil and gas reservoirs, coal formations, saline formations, basalt formations and the hydrate storage of CO_2 within the subsurface environment. Another option is deep ocean storage, however there is a constrain in this option (ocean acidification and eutrophication) which limits this technology and mineral carbonation. Details about all of these strategies and their progress can be found in reviews [4,5,32–36].

Mineral Carbonation

Developing a method for the secure sequestration of CO_2 in geological formations is one of the most serious difficulties that scientists have yet to overcome. Mineral carbonation is a method that has many advantages and has several features that make it unique among the other CO_2 storage procedures. First of all, the various minerals that may drive carbonation reactions are very common worldwide, contributing to a large storage capacity; second, the permanence of CO_2 storage in a stable solid form results in no CO_2 release from the storage site; and finally, the heat released from the reactions could theoretically be used as power resources [8,9,37]. In this method, CO_2 reacts chemically with calcium or magnesium oxides to form stable carbonate materials through the below reaction:

$$MO + CO_2 \rightarrow MCO_3 + heat,$$

where M is the divalent metal. The amount of heat depends on the metal and on the material containing the metal oxide.

The above reaction releases heat, which means that thermodynamic mineralization is realized at low temperatures, otherwise the calcinations take place. The big challenge in this method is to accelerate the carbonation, thus exploiting the appropriate amount of heat without causing problems in the environment [38].

Mineral carbonation can be carried out in two ways. The first one is the in-situ method where the CO_2 is injected into a geologic formation for the production of stable carbonates, such as calcite ($CaCO_3$), dolomite ($Ca_{0.5}Mg_{0.5}CO_3$), magnesite ($MgCO_3$), and siderite ($FeCO_3$). The products that are formed are thermodynamically stable, therefore, the sequestration is permanent and safe [39]. This method differs from the conventional geological storage because CO_2 is injected underground under the appropriate conditions to accelerate the natural process of mineral carbonization. The second one is the ex-situ method where the process takes place above ground in a processing plant [32,40]. The mineral carbonation process routes are described in detail by Olajire et al. [38].

In situ mineralization is preferable because there is no need for additional facilities and mining, the CO_2 is injected directly into porous rocks in the subsurface and reacts directly with the rocks. Moreover, there is no need for the transportation of the reactants, which could prove to be a difficult process. Finally, the amount of the minerals is larger when compared to minerals from industrial wastes [5,38]. However, there are also challenges with this method of mineralization, such as the critical choice of the rocks, which should contain metals and have the appropriate physical and chemical properties to accelerate the carbonation. Another challenge that scientists have to overcome is achieving carbonation acceleration and to utilize the heat released from the reactions [38]. The largest risk in this way of CO_2 storage is the leakage of the carbon [41–43], however, this risk may be limited by dissolving the CO_2 into water prior to or when it is injected into the rocks, as this form is denser than CO_2 in gas or in supercritical phase [44–46] Generally, the in situ method may be preferable for high volumes of CO_2 [47].

Ex-situ method has also some advantages: The availability of minerals at low cost and also their high reactivity when compared to natural minerals [38].

2.4. Minerals for Potential CO_2 Storage

Oxides and hydroxides of Ca and Mg have been proposed as suitable materials for mineral carbonation because they provide alkalinity. Although magnesia (MgO) and lime (CaO) are the most naturally occurring common earth metal oxides, they are usually bonded as silicates, such as olivine and serpentine (typically containing 30–60 wt% MgO) [39]. The carbonation of Ca is more effective, however, MgO is more common in nature [39]. Basalts and ophiolite rocks are enriched in magnesium, calcium, and iron silicates [7]. Among the silicate rocks, mafic and ultramafic rocks contain high amounts of Mg, Ca, and Fe, and have a low sodium and potassium content. Some of the main minerals in these rocks are olivines, serpentine, enstatite, and wollastonite [38]. Olivine, serpentine, peridotite and gabbro are mainly found in ophiolite belts geological zones according to Coleman et al. [48] and Nicolas et al. [49]. Table 1 indicates the composition of the most important minerals and their CO_2 sequestration characteristics [38,39]. R_{CO2} is the mass ratio of rock to CO_2 and R_c is the mass ratio of rock needed for CO_2 fixation to burned carbon. It can be seen that basalt consists of a relatively small amount of MgO when compared to dunite and serpentine, however, its capacity is higher, most likely due to the CaO, and also requires > 1.8 ton of rock per ton of sequestered CO_2:

Table 1. Composition of minerals and their CO2 sequestration characteristics (adapted from Lackner 1995 [9] and Wu 2001 [10])

Rock	MgO (wt%)	CaO (wt%)	Rc (kg/kg) Mass Ratio of Rock Needed for CO_2 Fixation to Burned Carbon	R_{CO2} (ton rock/ton CO_2) Mass Ratio of Rock to CO_2
Dunite (olivine)	49.5	0.3	6.8	1.8
Serpentine	40	0	8.4	2.3
Wollastonite	–	35	13	3.6
Talc	44	0	7.6	2.1
Basalt	6.2	9.4	26	7.1

Several studies and projects have been conducted in natural minerals for CO_2 sequestration. Table 2 indicates possible minerals for storage.

Table 2. List of natural minerals studied for mineral carbonation technology.

Minerals	References
Basaltic Rocks	Wu et al. [10], Gislason et.al [45], Matter et al. [50], Bassava-Redi et al. [51], Snaebjornsdottir, et al. [52], Rani et al. [53], van Pham et al. [54], Matter et al. [55], Schaef et al. [56], Goldberg et al. [57], Matter et al. [58]
Serpentine and Harzburgite	Koukouzas et al. [8], Dichicco et al. [37], Zevenhoven et al. [59], Veetil et al. [60], Krevor et al. [61], Turvey et al. [62], Klein et al. [63]
Olivine	Kwon et al. [64], Haug et al. [65], Eikeland et al. [66]
Dunite	Koukouzas et al. [8], Andreani et al. [67]
Peridotite Rocks	Andreani et al. [67], Falk et al. [68], Grozeva et al. [69]
Wollastonite	Min et al. [70], Xie et al. [71], Ding et al. [72]
Zeolite	Vatalis et al. [73]
Sandstone	Koukouzas et al. [74]
Forsterite	Kwak et al. [75]

3. Results and Discussion

3.1. CCS Technologies in Europe

The European energy policy established a strategy which promotes the use of renewable energies and the reduction of greenhouse gases with innovative technologies as carbon capture utilization storage (CCUS/SSC) [76].

Nowadays there are 78 commercial scale projects around Europe that are in various stages of development according to Scottish Carbon Capture and Storage (SCCS) [77]. The information about the projects are adapted from SCCS's map and indicated in Table 3.

A total of 36 of these projects have been cancelled/dormant or completed and only three are in operation, 21 are in a pilot phase, and 18 are in the planning/speculative stage or in design (Table 3). The UK hosts most of these plants (22), followed by Norway (12), The Netherlands (10), and Germany (9). The highest number of these plants (35%) do not use a storage site for the CO_2 but follow the process of utilization, 23% store the CO_2 in saline formations, and 15% in depleted oil and gas formations. Two of the three plants in operation (Snohvit in Norway and Sleipner in Norway) use saline formations as their storage sites and the Offshore Netherlands in The Netherlands uses depleted oil and gas formations. It is of great interest that all of the pilot plants utilized the captured CO_2, except for the Lacq CS Pilot in France, which stores it in depleted oil and gas formations, and the CarbFix in Iceland, which uses the mineral carbonization technique.

Table 3. Commercial scale projects of carbon capture and storage (CCS) technologies around Europe. Adapted from SCCS's map: www.sccs.org.uk/map.

Project	Location	Status/Started	Fuel	Storage
CarbFix	Near Hvergerdi, Iceland	Pilot/2012	Other	Mineral carbonization
Snohvit	Melkoya, near Hammerfest, Norway	Operational/2008	Gas	Saline formation
Tiller CO_2 Laboratory	Tiller, near Trondheim, Norway	Pilot/2010	Other	No storage
Industrikraft More CCS Project	Einesvagen, near Molde, Romsdal, Norway	Cancelled/Dormant	Gas	EOR Enhanced Oil Recovery
Technology Centre Mongstad		Pilot/2012	Gas	No storage
Kollsness CO_2 Storage Terminal	Rong, near Bergen, Norway	In design	Other	Saline formation
Sargas Husnes	Husnes, Hardangerfjord, Norway	Cancelled/Dormant	Coal	Unknown
Karsto	near Haugesund, Rogaland, Norway	Cancelled/Dormant	Gas	Saline formation
Klemetsrud	Klemetsrud, near Oslo, Norway	In planning	Other	Saline formation
Yara Porsgrunn Demonstration Project	Heroya Industrial Park, Porsgrunn, Norway	Cancelled/Dormant	Gas	Saline formation
Norcem CCS Demonstration Project	Brevik, Norway	In Design	Unknown	Saline formation
Frevar capture plant	Fredrikstad, Norway	Speculative	Other	Saline formation
Stepwise Pilot Plant	Lulea, Sweden	Pilot/2017	Other	No storage
Karlshamn Field Pilot	Karlshamn, Sweden	Completed	Oil	No storage
Nordjyllandsvaerket	Nordjylland, Denmark	Cancelled/Dormant	Coal	Saline Formation
Esbjerg Pilot Plant	Esbjerg, Denmark	Completed	Coal	No storage
Meri Pori CCS Project	near Pori, Finland	Cancelled/Dormant	Coal	Possibly EOR
Sleipner	Offshore Norwegian North Sea, Norway	Operational/1996	Gas	Saline formation
Whitegate and Aghada CCS Project	Whitegate, Co. Cork, Republic of Ireland	Speculative	Gas	Depleted oil and Gas
Acorn Project	St Fergus, UK	In planning	Gas	Unknown
Peterhead	Peterhead, Scotland, UK	Cancelled/Dormant	Gas	Depleted oil and gas
Scottish Carbon Capture and Storage	Edinburgh, Scotland, UK	Pilot	other	No storage
Caledonia Clean Energy Project	Grangemouth, Scotland, UK	In Planning	Gas	Unknown
Longannet	Fife, Scotland, UK	Cancelled/Dormant	Coal	Depleted oil and gas
Oxycoal2	Renfrew, Scotland, UK	Pilot/2009	Coal	No storage

Table 3. *Cont.*

Project	Location	Status/Started	Fuel	Storage
Hunterston	near Largs, North Ayrshire, UK	Cancelled/Dormant	Coal	Depleted oil and gas
Alcan Lynemouth	Lynemouth, Northumberland, UK	Cancelled/Dormant	Coal	Unknown
Blyth Power Station	Cambois, Blyth, UK	Cancelled/Dormant	Coal	Unknown
Teesside Collective	Teesside, UK	In planning	unknown	Saline Formation
Lotte Chemicals Carbon Capture Utilization and Storage CCUS Project	Wilton Site, Teesside, UK	In Design	Gas	Industrial Use
Teesside Low Carbon Project	Eston, Teeside, UK	Cancelled/Dormant	Coal	Depleted oil and gas
Liverpool-Manchester Hydrogen Cluster	Ince Marshes, Merseyside, UK	Speculative	Gas	Depleted oil and gas
Pilot-scale Advanced Capture Technology	Beighton, near Sheffied, UK	Pilot	Other	No storage
Ferrybridge	West Yorkshire, UK	Completed	Coal	No storage
Millenium Generation Project	Stainforth, South Yorkshire, UK	Pilot	Gas	No storage
Killingholme	Immingham, North Lincolnshire, UK	In planning	Coal	Saline formation
Aberthaw Pilot Plant	Aberthaw, near Barry, UK	Completed	Coal	No storage
Imperial College Carbon Capture Pilot Plant	South Kensigton Campus, London, UK	Pilot	Other	No storage
Tilbury Power Station	East Tilbury, UK	Cancelled/Dormant	Coal	Unknown
Kingsnorth	Kent, UK	Cancelled/Dormant	Coal	Depleted oil and gas
InfraStrata	Portland (exact location unknown), UK	Cancelled/Dormant	Unknown	Unknown
Offshore Netherlands North Sea, Netherlands	GDF Suez	Operational/2004	Gas	Depleted oil and gas
Eemshaven	Groningen, The Netherlands	Cancelled/Dormant	Coal	Depleted oil and gas
Buggenum Pilot Plant	Buggenum, near Roermond, The Netherlands	Completed	Coal	No storage
Air Products Rotterdam	Botlek, Rotterdam, The Netherlands	Cancelled/Dormant	Oil	No storage
Pegasus Rotterdam	Port of Rotterdam, The Netherlands	Cancelled/Dormant	Gas	Depleted oil and gas
Barendrecht Project	Port of Rotterdam, The Netherlands	Cancelled/Dormant	Oil	Depleted oil and gas
Rotterdam Backbone Project	The Rotterdam, The Netherlands	In planning	Other	Depleted oil and gas
Rotterdam Climate Initiative	Rotterdam, TheNetherlands	Cancelled	Other	Depleted oil and gas
CO_2 Smart Grid	Rotterdam, The Netherlands	Speculative	Other	Unknown
C.GEN Rotterdam	Europort, Rotterdam, The Netherlands	Cancelled/Dormant	Coal	Unknown
Rotterdam Opslag en Afvag Demo ROAD	Maasvlakte, Rotterdam, The Netherlands	Cancelled/Dormant	Coal	Depleted oil and gas

Table 3. *Cont.*

Project	Location	Status/Started	Fuel	Storage
Antwerp CCS Feasibility Study	Port of Antwerp, Belgium	Speculative	Unknown	Unknown
Leilac Pilot Plant	Lixhe, near Vise, Belgium	Pilot	Coal	No storage
Wilhelmshaven Pilot Plant	Wilhelmshaven, Germany	Pilot	Coal	No storage
Heyden Pilot Plant	near Minden, North Rhine-Westphalia, Germany	Pilot	Coal	No storage
Ketzin Pilot Injection Site	Ketzin, near Berlin, Germany	Completed	Unknown	Saline formation
Herne Pilot Plant	Herne, North Rhine-Westphalia, Germany	Pilot	Coal	No storage
Hurth IGCC	Hurth, near Koln, Germany	Cancelled/Dormant	Coal	Unknown
Niederaussem, near Koln, Germany	Niederaussem, near Koln, Germany	Pilot	Coal	No storage
Janschwalde	Brandenburg, Germany	Cancelled/Dormant	Coal	Saline formation
Staudinger Pilot Plant	Grosskrotzenburg, near Hannau, Germany	Pilot	Coal	No storage
EnBW Pilot Plant	Heilbronn, Germany	Pilot/2011	Coal	No storage
ArcelorMittal Florange	Florange, Moselle, France	In planning	Coal	Saline formation
C2A2 Field Pilot	Le Havre, Normandy, France	Pilot	Coal	No storage
Lacq CS Pilot	Lacq, Pyrenees-Atlantiques, France	Pilot	Gas	Depleted oil and gas
Compostilla Phase I	Cubillos del Sil, Ponferrada, Spain	Pilot	Coal	No storage
Puertollano	Puertollano, Ciudad Real, Spain	Completed	Coal	No storage
Belchatow	Lodz, Poland	Cancelled/Dormant	Coal	Saline formation
Kedzierzyn	Silesia, Poland	Cancelled/Dormant	Coal	Saline formation
CO_2SEPPL	Durnrohr, near Tulln, Austria	Pilot/2010	Coal	No storage
Retznei Oxyfuel Demonstration	Retznei, near Graz, Austria	In planning	Other	No storage
Porto Tolle	Porto Tolle, Veneto, Italy	Cancelled/Dormant	Coal	Saline formation
Colleferro Oxyfuel Demonstration	Colleferro, near Rome, Italy	In planning	Other	No storage
Brindisi, Puglia, Italy	Brindisi, Puglia, Italy	Pilot/2011	Coal	unknown
Delimara	Delimara, Marsaxlokk, Malta	In design	Coal	Depleted oil and gas
Getica CCS Demonstration Project	Turceni, near Targu Jui, Gorj County, Romania	Cancelled/Dormant	Coal	Saline formation
Maritsa	Stara Zagora Province, Bulgaria	Cancelled/Dormant	Coal	Saline formation

The Case of CarbFix (Iceland)

It focuses on mineral carbonation which is a new, environmentally safe, and low cost technique that will be studied further, in Europe. CarbFix is a project in Iceland that is injecting solutions of mixed CO_2 and H_2S into basaltic rocks (basaltic lava flows and hyaloclastite) at 1000 m. The field site is situated in SW Iceland, close to a geothermal power plant that produces up to 30,000 tons of CO_2 per annum and is estimated to increase. The source of CO_2 is the geothermal gas which is a byproduct of the geothermal steam production [55]. The project started in 2007 and has been in operation since 2012. It has been estimated that in 2017, it injected about 10,000 tons of CO_2. The percentage of CO_2 that has mineralized as carbonates in the basalt rocks has been found to be almost complete (95%) within two years (Carbon Capture and Storage Association). The existence of a large available area of basaltic rocks associated with the rapid carbonation reactions may result in a safe and permanent solution.

3.2. CO_2 Storage in Greece

The biggest source of CO_2 in Greece is the lignite fired power plants in western Macedonia. Greece ranks second in the European Union and sixth worldwide in terms of lignite production. Today, the eight PPC lignite power plants represent 42% of the country's total installed capacity and generate nearly 56% of the country's electrical energy according to the website of the Public Power Corporation S.A. Hellas. The use of this important energy source is facing a serious challenge, due to the vast amounts of CO_2 emitted into the atmosphere during lignite combustion. The CO_2 emissions from fuel combustion in Greece, was found to be 64.6 million tons, including a high amount from the lignite fired power plants [2]. The reduction of CO_2 emissions in the atmosphere is one of the biggest challenges that scientists have to face. The goal of the Paris Agreement is to keep the global temperature rise below 2 °C compared to pre-industrial levels, as well as to limit the temperature increase to no more than 1.5 °C, thus aiming to reduce the risks and impact of climate change [3]. The CCS technologies in Europe as above mentioned are far from the Greek power plants and the transportation of CO_2 is a very difficult process. As a result, an appropriate CO_2 storage site in Greece would present an effective solution.

There are only a few studies conducted on CO_2 storage through the application of the CCS technique in Greece as indicated in Table 4. One potential storage site in the oil and gas fields lies in Prinos, Kavala in NE Greece. Furthermore, an estimation was conducted through a model where the potential storage capacity in the Pentalofos (Tsarnos and Kalloni members) and Eptahori reservoirs in NW Greece was found to be 728 billion tons of CO_2 for both storage sites [78]. In Prinos (Thassos–Kavala path), a hydrocarbon field offshore in Northern Greece that had a monitoring system that simulated a potential CO_2 leakage from the Prinos field was investigated and found that CO_2 reached the seabed in approximately 13.7 years after the injection and it reaches its peak after 32.9 years. The model results showed that CO_2 would flow towards the Natura protected areas only in only five days after the leakage, and during this period, the authorities need to take appropriate measures to avoid environmental problems. Thus, a possible leakage would affect the environment [79]. However, the consequences of a CO_2 leakage are considered to be limited, from which the ecosystem is capable of recovering. Finally, the amount to operate this system was calculated to have costed 0.38$/ton of CO_2 and 0.45$/ton of CO_2 for EOR [79].

Table 4. List of sites in Greece studied for CCS plants.

Potential Storage Site	References
Prinos, Kavala in northern Greece, Pentalofos, Eptahori, NW Greece	Tasianas et al. [78]
Evros, northern Greece	Vatalis et al. [73]
Pentalofos and Tsotili, NW Greece	Koukouzas et al. [74]
Vourinos, western Macedonia	Koukouzas et al. [8]

Vatalis et al. [73] proposed the storage of CO_2 in the known deposit of zeolite in Evros (Northern Greece). Koukouzas et al. [74] concluded that the Pentalofos and Tsotyli sandstone formations could be a potential CO_2 storage site under specific conditions. This approach needs further investigation.

Another promising technique for CO_2 storage without such environmental risks is mineral carbonation. A study was conducted on the storage of captured CO_2 in magnesium silicates. For the experiment, samples from ultramafic rocks from Mount Vourinos in Western Macedonia, Greece, were used in companion with the aqueous technique. The results indicated limited carbonation, however, this situation will likely change under different experimental conditions. For example, a longer reaction time, the particle size, and the discharge of impurities which poison the reaction, would probably improve the carbonation [8].

Generally, mineral carbonation is a new CCS process that promises the permanent storage of CO_2. The most important aspect is that specific conditions need to ensure that the carbonates formed are environmentally benign and geologically stable. Considering the geological forms that are appropriate for CO_2 storage through mineral carbonation, Greece could be a potential site for CO_2 storage because all of these geological forms could be found throughout continental Greece. The most capable sites for CO_2 injections are indicated in Table 5. Ultramafic lavas associated with high basaltic dykes are found in the Othris Mountains in Central Greece [80–84]. In the Othris ophiolite complex, olivine phyric lavas from the Agrillia area (about six Km NW from Lamia) and high MgO basaltic dykes from Pournari area (about 31 KM NW from Lamia) have been found. The majority (in wt%) of elements determined for ultramafic lavas from the Agrillia area showed the highest values for SiO_2, MgO, CaO and FeO in all sample cases and high–Mg basalts from Pournari showed the highest values for SiO_2, FeO, MgO and CaO in all sample cases [80]. Furthermore, the lower unit of the Pindos ophiolitic belt is mainly composed of basaltic rocks [85] Gabbroic and basaltic rocks are also found in the Serbo-Macedonian (Volvi and Therma bodies) and western Rodopi (Rila mountains) massifs of Bulgaria and Greece [86,87]. Finally, basalts can be found in ophiolitic rocks of the Attic-Cycladic crystalline belt. According to Stouraiti et al. [88] basalts exhibiting high MgO concentrations in Paros, western Samos (Kallithea), Naxos, central Samos, Skyros, Tinos, and S. Evia have been found. Moreover, basalts have been found on the Acrotiri Peninsula, Santorini, Greece [89], as well as in Kos–Nisyros [90]. However, the major factor that eliminates the potential for CO_2 storage in these last areas is that they are islands with limited storage areas and the transportation of CO_2 in these cases would be a very difficult and high cost process.

Ophiolites in Greece are widespread, and are mostly exposed in central and northern Greece. Large ultramafic bodies are found in the East Othris ophiolite belt. It has been shown [91,92] that in the Vrinera ophiolitic unit, the ultramafic rocks consist of serpentinized harzburgites and are found below gabbros and diorites. The ophilithic units of Eretria, Aerino, and Velestino consist mainly of serpentites, which is the same case in the southern part of Aerino. Finally, serpentinites can be found in the ophiolitic mélange of Ag. Giorgios, but it is rather small (2 km^2). The ophiolite units of two Greek islands, Evia and Lesvos, comprise of amphibolitesm, and below them lie ultramafic masses that consist of serpentinized harzburgites, patches of dunites and serpentinized depleted iherzolites and harzburgites, respectively [93]. A study that was conducted in the east part of Thessaly, Central Greece showed that the metaophiolites of this region consisted mainly of serpentinites and metabasites [94] The Pindos ophiolite complex in NW Greece is mainly comprised of large harzburgite-dunite masses > 1000 km^2 in the mantle peridotites [95–97]. Among the Western Hellenic Ophiolites is Vourinos ophiolite complex in Western Macedonia, NW Greece, represents a mid-Jurassic complete lithospheric slab about 12 km thick and 400 km^2 and consist of depleted harzburgite mantle which hosts bodies of dunite ranging in size from several meters to kilometers in scale length [8,96,98–100]. Several studies have been conducted in Vourinos and showed that dunite was surrounded by serpentinized harzburgites with some lenses of serpentinized dunite [97]. Furthermore, the Koziakas mountain ophiolite in western Thessaly, also belongs to the West Greek ophiolite belt and is comprised of mantle peridoites with harzburgites and secondary plagioscale bearing Iherzolites [97,101].

Table 5. The appropriate geological forms for mineral carbonation in Greece.

Geological Form	Sites in Greece	References
Ultramafic lavas with basaltic dykes	Othris Mountains, Central Greece	Baziotis et al. [80], Saccani et al. [81], Tsikouras et al. [82], Valsamia et al. [83], Paraskevopoulos et al. [84]
Basaltic rocks	Pindos, NW Greece	Saccani et al. [85]
Gabbroic and basaltic rocks	Volvi and Therma bodies in western Macedonia, Northern Greece	Bonev et al. [86], Bonev et al. [87]
Gabbroic and basaltic rocks	Western Rodopi massifs (northern Greece)	Bonev et al. [86], Bonev et al. [87]
Basalts	Paros, Western Samos, Naxos, central Samos, Skyros, Tinos and S. Evia, Greek Islands in Central and Southern Aegean	Stourati et al. [88]
Basalts	Acrotiri Peninsula, Santorini and Kos-Nisyros, Greek Islands in S. Aegean	Mortazavi et al. [89], Bachman et al. [90]
Ultramafic rocks consist of serpentinized harzburgites	Vrinera ophiolitic unit, East Othris, central Greece	Magganas et al. [91], Koutsovitis et al. [92]
Ophilithic units consist of Serpentites	Eretria, Aerino, Velestino, central Greece	Magganas et al. [91], Koutsovitis et al. [92]
Amphibolites and below them underlie ultramafic masses which consist of serpentinized harzburgites, patches of dunites and serpentinized depleted iherzolites and harzburgites	Evia, island in central Greece and Lesvos, island in Northern Aegean	Gartzos et al. [93]
Metaophiolites consist of serpentinites and metabasites	East part of Thessaly, Central Greece	Koutsovitis et al. [94]
Ophiolite complex is comprised of harzburgite-dunite masses in the mantle peridotites	Pindos, NW Greece	Economou et al. [95], Rssios et al. [96], Rigopoulos et al. [97]
Harzburgite mantle which hosts bodies of dunite	Vourinos, NW Greece	Koukouzas et al. [8], Rassios et al. [96], Rigopoulow et al. [97], Tzamos et al. [98], Ross et al. [99], Tzamos et al. [100]
Ophiolite is comprised of mantle peridoites with harzburgites and secondary plagioscale bearing Iherzolites	Koziakas mountain ophiolite, western Thessali, Central Greece	Koukouzas et al. [8], Rigopoulos et al. [97], Tzamos et al. [98], Ross et al. [99], Tzamos et al. [100], Pomonis et al. [101]

There are several sites in Greece that could be CO_2 storage sites, since their underground is home to rocks that are rich in olivine, serpentine, harzburgites, dunites, peridotites and basaltic glass which include high amounts of Mg, Ca, and Fe oxides and hydroxides. As previously mentioned, the islands could not be part of these sites as the CO_2 transportation cost would prove too high. Greece has several industries that produce high amounts of CO_2 (the total CO_2 emissions from Greece in 2016 was 67,870 thousand tons according to World Data Atlas) and mineral carbonation technology would be a sustainable solution for this problem, taking into account that there are already appropriate geological forms capable of permanent and safe storage. According to Table 5, Mount Orthis in central Greece, Western Rodopi in northern Greece, Pindos in NW Greece, Vourinos in western Macedonia, as well as Koziakas in western Thessaly could be sites for CO_2 storage. The most suitable CO_2 storage site should be established in basins where rocks containing the appropriate porosity exist, and are close to power stations or industries to avoid high transportation costs. The power stations in Greece are placed mainly in the Ptolemais–Amynteo lignite center (western Macedonia, Northern Greece).

After conducting a literature review in near regions, it indicated that the Mount Pindos ophiolite and mainly the Vourinos ophiolite complex (which extends SW of Kozani covering an area of 450 km^2) are situated very close to the power station and are comprised of harzburgite-dunite masses in the mantle peridotites and dunite surrounded by serpentinized harzburgites with some lenses of serpentinized dunite, respectively. These natural minerals are rich in the oxides and hydroxides of Ca, Mg, and Fe, representing the appropriate materials for mineral carbonization. Mineral carbonation is a permanent and environmentally safe CO_2 storage technology which does not incur long term liability (avoiding the challenge of degrading the environment) or monitoring obligations. Taking into account that these two areas are very close to the power stations, thus limiting the CO_2 transportation costs, this method could be a potential technique for reducing CO_2 emissions, therefore fulfilling the goals of the Paris Agreement. However, it was also found that there are other potential sites capable for mineral carbonation in continental Greece (e.g., the Orthis ophiolite belt), but further economic research should be conducted in order to estimate the CO_2 transportation costs for comparison with the profits of the operation of such technology.

4. Conclusions

Carbon capture and storage is a key climate change mitigation technology. This work presents a review of state-of-the-art developments in CO_2 capture, transport, and storage and discusses critical issues that have been solved. Mineral carbonation of CO_2 is gaining more and more ground as an important CCS method that provides an alternative for CO_2 storage in underground formations. In addition, the European commercial scale projects of CCS in their stage of development were highlighted and demonstrated that 36 of these projects have been cancelled or completed, 18 are in planning or in design, only 3 are in operation, and 21 are in a pilot phase. The CarbFix project which is the only one case of mineral carbonation in Europe is discussed in detail. The goal of this research is to perform an investigation for the possibility of CO_2 storage through mineral carbonation in Greece. The mineralogical composition of basaltic rocks in Othris Mountains (Central Greece), in Pindos (NW Greece), in Western Rodopi massifs (Northern Greece) and in several islands in the Aegean, such as Paros, Western Samos, Skyros, Tinos, S. Evia, Santorini, Kos and Nisiros, as well as of serpentites and harzburgites in East Othris (Central Greece), in Evia and Lesvos (islands in Aegean), in east part of Thessaly (Central Greece), in Pindos (NW Greece), in Vourinos (NW Greece), and in Koziakas (Central Greece) indicates that they could serve as potential CO_2 storage sites. Taking into account that the biggest source of CO_2 in Greece is the lignite fired power plants in NW Greece in addition to the high cost of CO_2 transportation, the research concluded that the mountain Pindos ophiolite complex and mainly the Vourinos ophiolite complex which are found near the Greek power plants could be potential CO_2 storage sites for mineral carbonation. Further research for the geology, the chemical and hydrodynamic characteristics below ground, as well as a financial study, should be conducted in the future in order to ensure that the proposed solution is economically and technologically viable.

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