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MSc Course in Petroleum Engineering

# **The role of Geosciences in Geothermal Resources and CCS.**

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## ***Abstract***

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Geothermal resources and Carbon Capture Sequestration (CCS) are upcoming and innovative technologies, while also being environmentally friendly. Geothermal resources rely on geothermal energy, which is Earth's natural internal heat. Geothermal energy is clean, renewable, sustainable, and available 24/7. This heat is used for many purposes, such as power generation and district heating/cooling, instead of fossil fuels. As a result, carbon footprint is lower, and the emission of greenhouse gases is preserved at low levels. CCS, on the other hand, prevents CO<sub>2</sub> from releasing into the atmosphere and mitigate global warming, which is responsible for climate change.

The role of geosciences, in Geothermal Resources and Carbon Capture Sequestration, is significant, with Geology having the main role. In Geothermal resources, geology is responsible for their existence and can provide crucial information during many stages, like exploration, economic appraisal, and production. While, in CCS, geological setting is very important for sustainable storage of CO<sub>2</sub>, into the geological formations, to prevent global warming.

As it seems Geothermal Resources and CCS are becoming more favorable and profitable, over time, especially with the development of new technologies and solutions. Greece appears to have huge potential in many locations for both projects.

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## ***Introduction***

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In this thesis we are going to deal with two different technologies/projects, Geothermal Resources and Carbon Capture Sequestration, which are the key to the future of a safer environment and of the economy. The important part in this assessment is the contribution of Geosciences in each case. Especially Geology has the primary role in both cases, followed by Geochemistry, Geophysics, GIS, and Hydrology etc.

Globally, over the years, more and more countries have started to adapt and develop Geothermal and CCS projects. The development of technology has given the opportunity to access areas that previously were impossible, increasing that way the potential for successful and sustainable projects.

Greece has shown a huge potential in many locations for Geothermal Resources and CCS. These locations and their characteristics will be mentioned below.

# 1. Geothermal Resources

## 1.1 Geothermal Energy

Geothermal Energy is Earth's (geo) natural internal heat (thermal) [42], which is estimated to be 5,500°C, which reaches Sun's surface temperature [56]. This heat is clean and sustainable [42]. The heat derives from the thermal energy that was produced during Earth's formation, from gravitational pressure of the Earth itself, and from the decay of radioactive elements (U, Th) in Earth's crust, [9,29,56,57] and mantle, and transferred to the subsurface by conduction and convection [56]. Convection of the mantle is the primary driving force of tectonic plate movement [29]. Heat is transferred from the mantle to the crust and then through conduction to the surface and released to space [29]. Since heat is transferred as mentioned above, temperature rate will almost always increased with depth, which is referred to as Geothermal gradients [56].

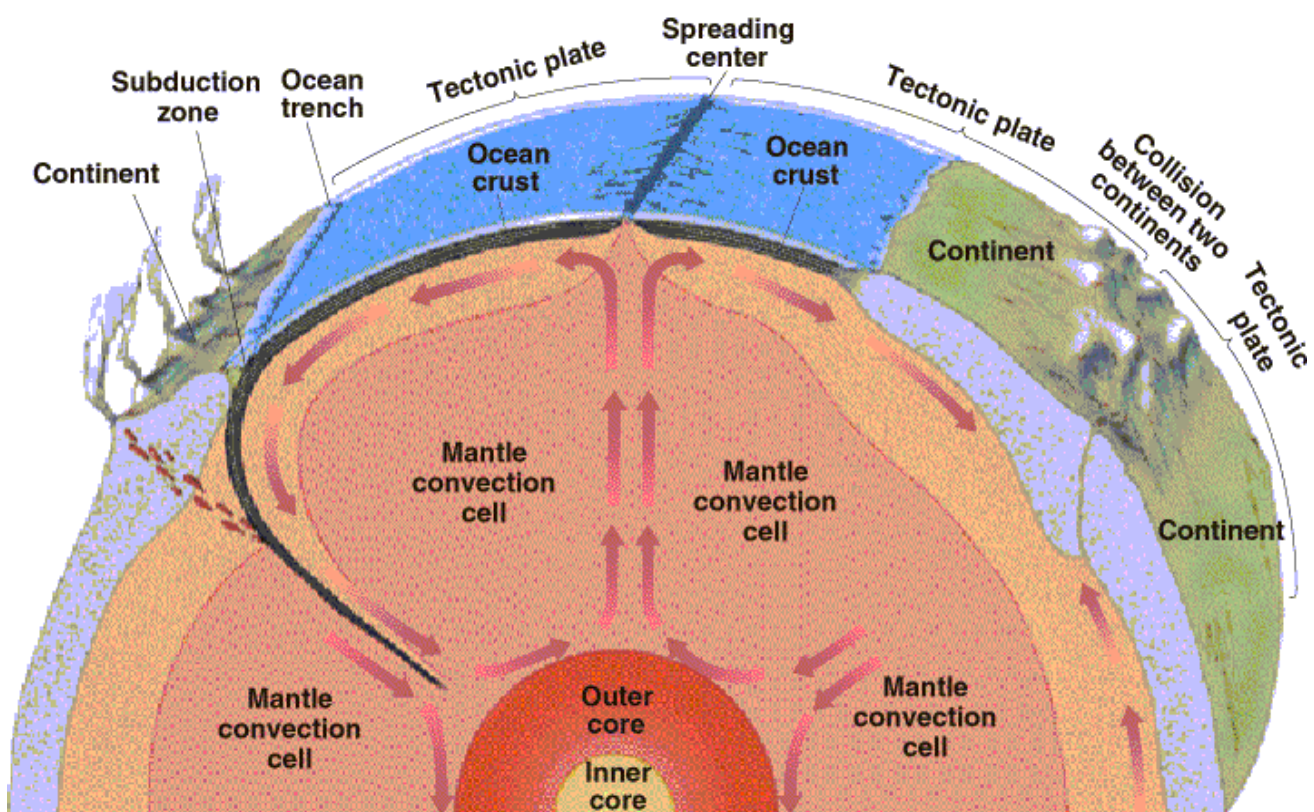


Figure 1: Mantle convection may be the main driver behind plate tectonics. Courtesy University of Sydney [29]

Nonetheless, there are cases where there are higher temperatures at shallower depths, such as Mid Ocean Ridges, from the rise of magma. This process will lead to the continuous formation of new crust and the heating the rocks, near it [29].

Geothermal energy could be transferred or removed from rocks or sediments, so it can be utilized for many purposes [9,57]. Geothermal energy can be used as energy source for

power generation [42], heating and cooling of buildings, and industrial purposes like fruit and vegetable cultivation etc. [56]. The thickness of continental crust regulates the usage of deep-sourced heat for power generation or commercial heating [9,57]. An alternative method, is to use store low-grade heat, in subsurface at shallow depths, less than 200m, from solar radiation. The heat is absorbed in the ground, which acts like a solar/thermal battery. At those depths, the temperature shows stability and indicate the average annual air temperature. The utilization of this heat, necessitates the usage of a heat pump, in order to be able to be distributed in buildings during winter, and inject the redundant back to the ground during summer [9,57].

Geothermal energy is a clean, renewable resource that can be found in geologically favorable places around the world. This energy can be exploited from underground reservoirs, containing hot rocks saturated with water and/or steam, through boreholes of 2 or more km. Then the hot water is transferred to the power plant and used as kinetic force, for power generation [40] The term renewable derives from the fact that after exploiting Earth's interior heat, which is considered abundant, then once the water is used and cooled, is piped back to the reservoir [40]. Geothermal resources vary from shallow ground to steam, hot water and hot rock accessed by drilling wells up to thousands of feet beneath Earth's surface [42].

Nowadays we can utilize geothermal heat to produce energy via power plants, Enhanced Geothermal Solutions, Direct use and Geothermal Heat Pumps. Geothermal energy has proven to be a reliable and non-polluting source of power and after considering its high availability and independence outer sources, it is the key to a sustainable energy future [56].

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## ***1.2 Utilization of Geothermal Resources***

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Geothermal energy can be utilized for electrical power generation and for other types of direct use applications (e.g., space heating for buildings or greenhouses, for food production, such as food dehydration etc.) Geothermal is unique energy as it provides a base-load alternative to fossil fuels usage [40].

**Geothermal resources with [40]:**

- high temperatures, greater than 150°C are used for electricity generation
- medium-to-low temperatures, below 150°C are suited for industrial applications, that require heat.
- low-temperature binary systems of 70°C, can also be used to generate electricity



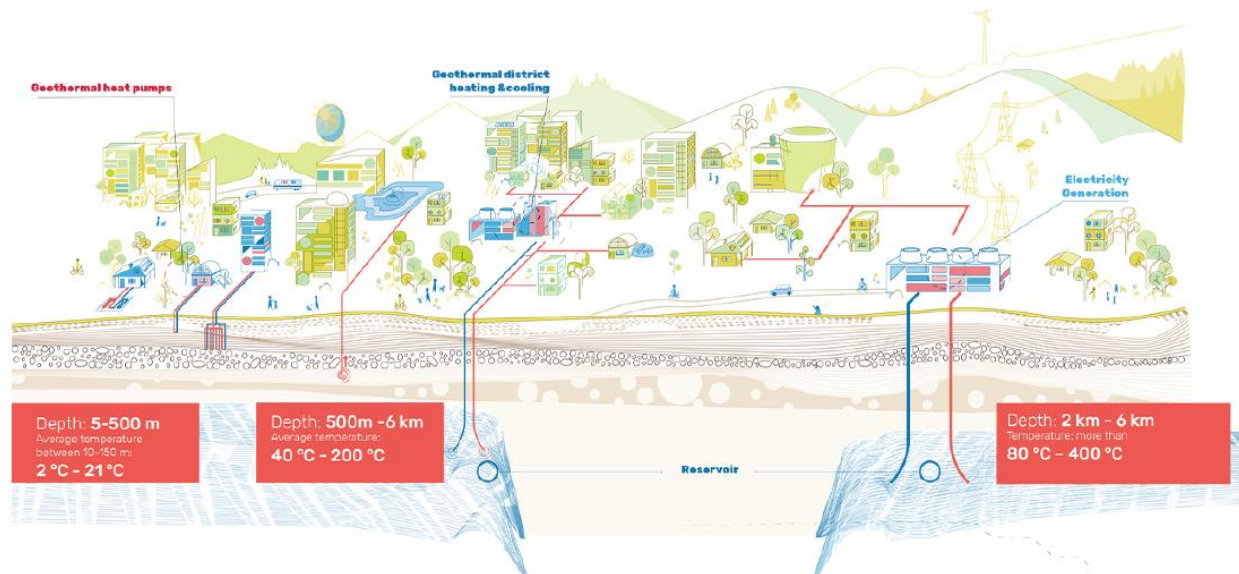


Figure 2: Utilization of Geothermal Resources [26]

## Electricity Generation

Deep geothermal reservoirs with extremely high temperatures are used for electricity generation [26,42]. However, temperature and depth, are dependent on the regions and the characteristics of the field [26]. A geothermal system with prevailing temperature at 150°C or above, can be utilized for large-scale power generation, to supply cities and heavy industries, but by preserving a low environmental impact [42]. In this kind of geothermal reservoirs, to produce hot water and steam, wells must be drilled till a depth of 3km [40]. Hot water and steam piped to the surface [26], work as carriers of geothermal energy, which is converted into electricity, using power plants [40]. Power plants have a capacity of 1-40 Mwe to produce baseload electricity [26].

Geothermal power is renewable and sustainable energy source and with the right handling it can be used for decades. Earth generates heat 24/7, so power generation can have the same production rhythm [29]. Power plants can operate 24/7 with consistency and stability[26,42], regardless of the prevailing environmental conditions, the unpredictability and voltage swings, that they will probably face. Geothermal plants can also quickly adjust to the changing needs of the power system [42]. Moreover, their high capacity, makes them reliable [29].

Power plants can either produce electricity directly from high temperature steam (flash technology), or from geothermal water with intermediate temperature of 70-170°C (binary technology). After the usage of the geothermal fluids, they are injected back to the reservoir, to preserve its pressure. These fluids contain most of the potential contaminants, so in that way geothermal power plants meet clean air standards. Gases such as CO<sub>2</sub>, are not produced during the operation of power plants, but the exist as natural trace constituents in all geothermal systems [56]. Meaning that geothermal electricity has a small footprint, since it is low emission and low polluting, with waste products only hot water, silica and calcite [29]. Geysers is the largest geothermal electricity generator, in the world, with a capacity of over 2000 MW [29].

## **Direct uses**

Geothermal resources are directly used for industrial purposes, other than power generation [29,40]. For direct uses, 50-150°C temperature fluids are required, with usually occur within 2-3km depth. Worldwide, there is a consumption of over 107,000 MWth and more than 283,000 GWh per year for these purposes [29]. A numerous number of countries report the use of geothermal energy for these kind of uses. Since the geothermal fluid temperature in direct uses is much lower than for electricity generation, it makes geothermal application very promising [56].

### ▪ **Geothermal district heating and cooling**

Space and Water Heating is the main direct use type of Geothermal system [56], which can be directly achieved by using geothermal water at temperatures of 100°C or below boiling. Associated uses are District Heating and GeoExchange [42]. A geothermal district heating and cooling system, can be applied according to energy needs, in residential buildings, greenhouses, industries, offices, etc [26]. Geothermal energy/heat derives from underground reservoir of water and hot rocks and is distributed into buildings or processed by industries [26]. The drilling depth for European heating networks from 1 to 3km (Paris, Munich, Milan, Southampton etc.) [26]. It is believed that in the future, these networks will be able to provide energy for 25% of the European population [26].

### ▪ **Other uses**

Geothermal energy can be used in many other applications including:

- Aquaculture - Fish Farming: Geothermal heat is used for water warming, because it contributes to the growth of smolt, prawns, eels, and alligators [42].
- Greenhouses - Agriculture: In cases where geothermally heated water, is too cool to be used for power generation, as an alternative, it can be used for vegetable, fruit and ornamental flower growth. Iceland has already adopted this procedure, leading to lower import costs for these products [42].
- Desalination [29].
- Heating swimming pools, health spas [29].
- Industrial processes: where heat rather than electricity is needed [29]. Many industries take advantage of the geothermal systems for cooling or heating processes, and therefore decrease operational costs [42].
- Other like, production of consumer goods, food processing [56], timber and paper processing, refrigeration, equipment sterilization, milk pasteurization [29].
- Production of Green Hydrogen, for industrial uses and transportation fuel [29].



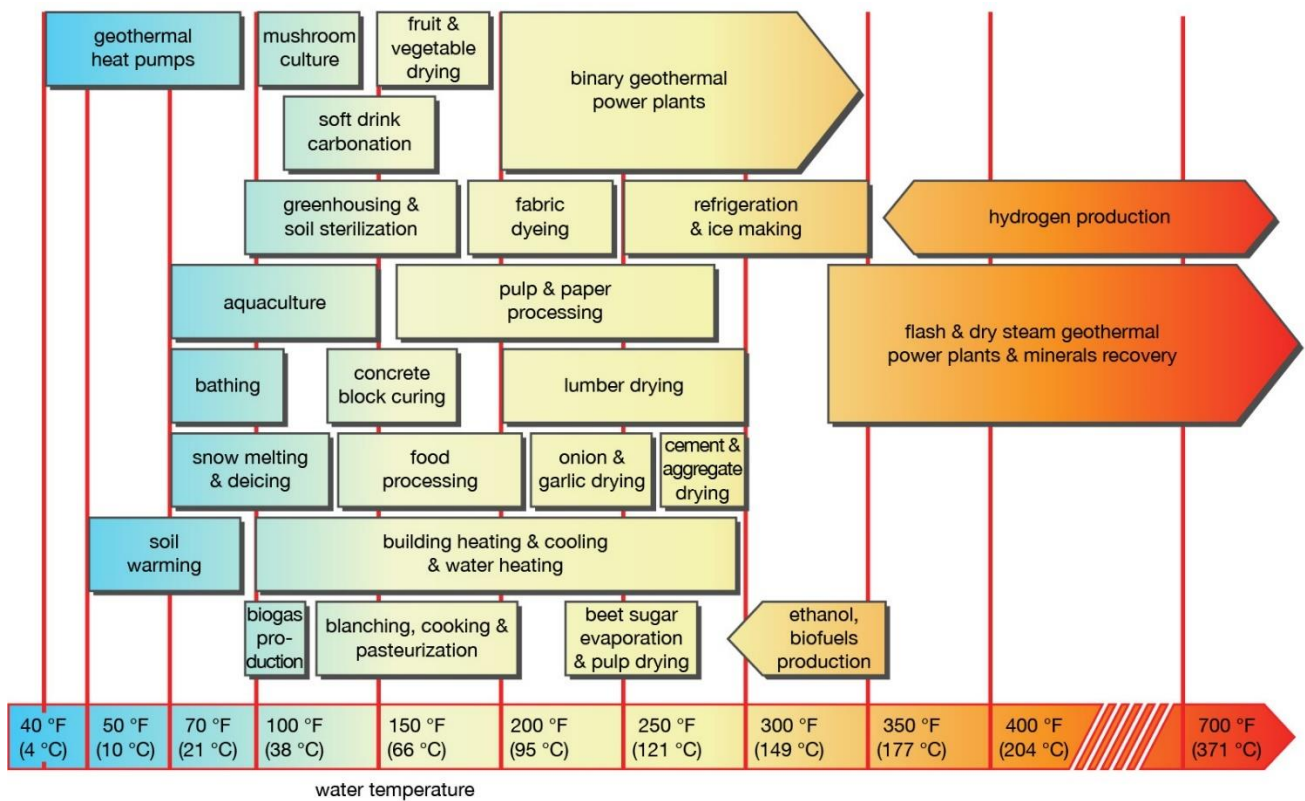
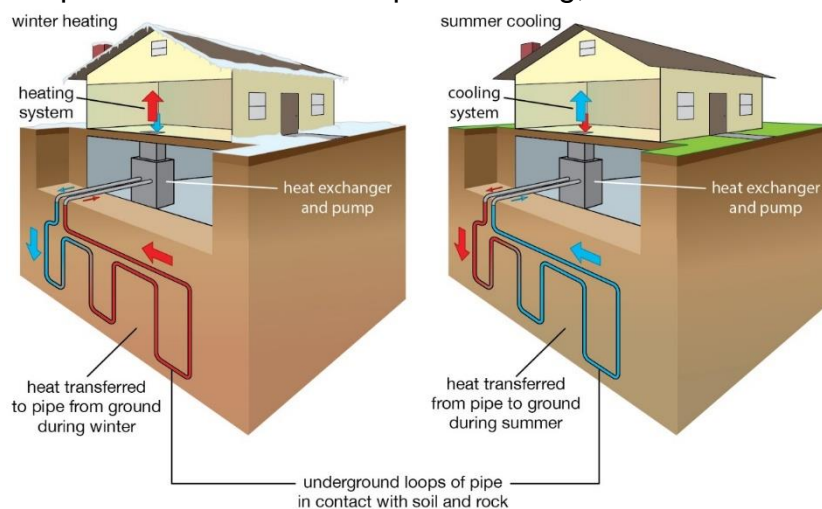


Figure 3: Geothermal energy uses. Courtesy Geothermal Education Office, Tiburon, California, USA [29]

## Geothermal Heat Pumps

Geothermal Heat Pumps (GHP or GSHP) [56], offer the most efficient and cheapest energy in Europe, as they take advantage of the constant underground temperature [26,40]. GHP take advantage of the relatively stable temperature conditions that prevail near surface [29]. They are mainly used for heating and cooling, but also for hot water provision for commercial use [26,40]. The heat is provided to the buildings through boreholes reaching the reservoir [26]. GHP mainly use temperatures of 10-20°C. However, when the temperature is too low for space heating, it can still be utilized for smaller applications.



Dealing with reservoir temperatures of 5-30°C, it is considered as a routine. But the majority of systems are quite shallow (~6m) where the temperature is 10-16°C [29]. Reversible heat pumps can be used for cooling or heating, depending on the season [56]. GSHP require 25-50% less electricity and emit 44-72% less greenhouse gases [29].

Figure 4: Residential heat pump diagram. Courtesy Encyclopaedia Britannica, Inc (2012) [29]

## Global Geothermal Use, 2015

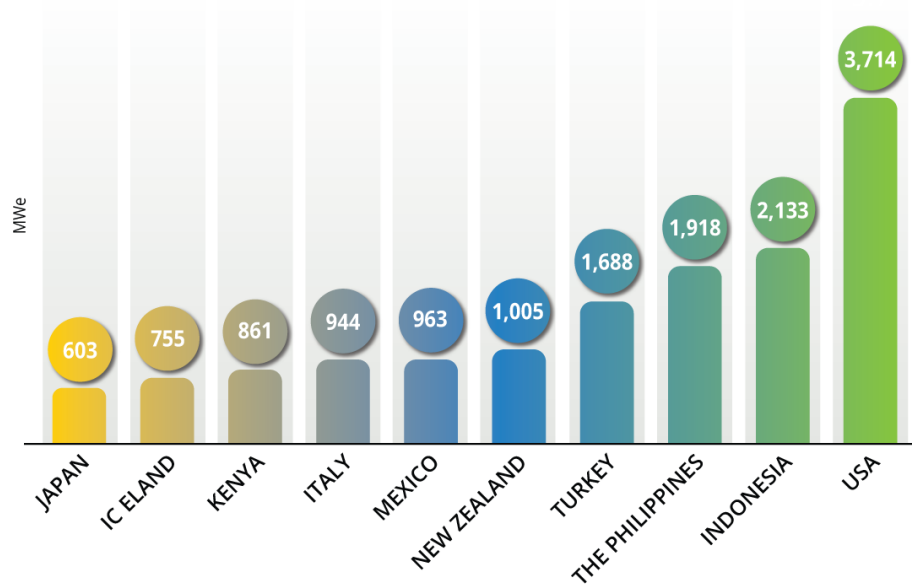


Figure 5: Global Geothermal Use, 2015 [56]

## Top 10 Countries Geothermal Countries 2020

Installed Capacity in MWe Year-End 2020

**Total 15,608 MW**



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### 1.3 Advantages and disadvantages of Geothermal Resources

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#### Advantages

- **Environmentally Friendly:** Low carbon footprint and minimal pollution, when compared to fossil fuels [80,120].
- **Fossil fuel free:** since geothermal systems operate without fossil fuel burning (coal, oil, and gas), the emission of greenhouse gases is preserved at low levels [42]. It is the solution for greenhouse gas emissions reduction in Europe [26]. Only renewable source which contributes to the **decarbonisation** of the electricity, heating & cooling, and transport sectors simultaneously [26].
- **Renewable:** geothermal energy will be produced as long as Earth exist, and the reservoirs are naturally replenished[120]. Geothermal energy is an endless source [26].
- **Sustainable / Stable/ Reliable:** unlike solar or wind energy, geothermal energy is always available, 24/7, making her reliable [42,120]. and able to meet consumers demands [26]. Geothermal energy is consistent, with continuous and flexible baseload power [42]. Furthermore, is easier to calculate, since it does not show the same variations as the other types of energy sources, leading to accurate predictions regarding the energy production of a geothermal plant [120].
- **No fuel requirements:** geothermal energy is natural, so there is no need of fuel like in the case of fossil fuel extraction [120].
- **Huge potential:** even though most of the reservoirs are not exploitable, ongoing research and development in the industry, will increase the exploitations. It is estimated that a power plant could provide 0.0035-2 terawatts, when worldwide energy consumption is estimated at 15 terawatts [120]. It is assessed that Geothermal energy will be capable of satisfying ~25% of European energy needs by 2030 [26].
- **Rapid Evolution:** new technologies will improve and grow this industry, leading probably to zero disadvantages [120].
- **Sustainable investment:** it is the cheapest renewable energy, since after the initial installation investment, the operating costs are considered very low and predictable [26]. Geothermal investment is very profitable and it will continue to be [42].
- **Job booster:** Power plants occupy 1.17 persons/ MW, and by considering governmental, administrative and technical jobs, the number increases to 2.13 [42].

## Disadvantages [120]

- **Location Restricted:** geothermal resources can be accessed only at specific locations, constraining the development of power plants and the exploitation on many fields.
- **Environmental impacts:** many gases are released during drilling, which increase near the geothermal plants, but these emissions are far lower than from fossil fuels.
- **Earthquakes:** drilling procedures are capable of triggering earthquakes. Especially enhanced geothermal power plants, which inject water into the wells to maximize the exploitation of resources. However, the effects of these earthquakes will be limited since geothermal plants usually constructed far from population centers.
- **High costs:** prices for power plants of 1 megawatt capacity vary between 2-7 million dollars, but it will be a very profitable investment.
- **Sustainability:** Geothermal fluids need to be injected into the reservoir faster than it is depleted. Meaning that proper management of geothermal energy is required to maintain its sustainability.

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### **1.4 Geothermal Energy Resources vs Oil & Gas characteristics**

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Stellae Energy [113], mentions the similarities and differences between Geothermal Energy Resources and Oil & Gas characteristics

<b>Oil &amp; Gas</b>	<b>Geothermal resources</b>
<b>Source rock:</b> fine-grained sediments with sufficient amounts of organic matter, which generate and release hydrocarbons able to migrate upwards	<b>Heat Source:</b> volcanic/magmatic sources along plate boundaries; abnormally high heat flow from thinner crust areas or granitic igneous intrusions
<b>Fluids :</b> hydrocarbon oil & gas and water	<b>Fluids:</b> mineralized water / brines or surface injected fluids
<b>Reservoirs:</b> accumulations of hydrocarbons contained in porous or fractured rock formations (i.e. sandstone, limestone)	<b>Reservoirs:</b> Permeable Hydrothermal (wet, able to be produced and reinjected) or Fractured Rock (dry, natural or induced, able to have surface fluids injected and circulated)
<b>Trap/Seals:</b> structural or stratigraphic traps with cap rock seals preventing further hydrocarbon migration	<b>Traps/Seals:</b> Thermal seals including impermeable rock
<b>Surface Indicators:</b> oil & gas seeps / releases, acoustic plumes	<b>Surface Indicators:</b> thermal gradients, hydrothermal features
<b>Exploration:</b> Geophysical (Gravity, 3D Seismic), Wells.	<b>Evaluation:</b> Geophysical (AMT, Gravity, some Seismic), Wells.

Table 1: Geothermal Energy Resources vs Oil & Gas characteristics [113]

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## 1.5 Geology

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Geology plays an important role in geothermal resources development and exploration [27]. Geology can provide potential targets, information about permeability and the distribution of subsurface rocks and develop conceptual models of geothermal systems, since in the first steps of geothermal exploration, data limitation leads to the usage of geothermal systems at similar environments. Also, it can develop quantitative reservoir models [27].

### Heat flow and plate tectonics

The total heat flow from Earth's interior to surface, is estimated at 47 TW, with the average crustal heat flow to be at 91.6 mW/m<sup>2</sup>. However, the crustal heat flow is depending on the geological environment, with continental crust having 70.9 mW/m<sup>2</sup> and oceanic one 105.4 mW/m<sup>2</sup> [27].

Along the stable areas of Earth's shallow crust, heat flow is responsible for the development of geothermal gradients of about 30°C/km. On the contrary, at tectonically active zones, the geothermal gradient can reach up to 500°C/km [27].

Geothermal system classification depends on the reservoir temperature, fluid type and heat transfer mechanisms [27]. Heat is transported closer to the surface where it can be economically accessed by drilling wells [114].

### Heat sources [114]

Magmatic sources which were not able to reach surface or after reaching surface they were buried by sedimentary processes but continue to produce heat. For example, igneous intrusions (dykes and sills). Likewise, granitoids are granitic intrusions which are revealed through geological processes or erosion. All these intrusions work as pathways for the upward movement of heat and hydrous melts. These intrusions contribute to hydrothermal mineralization and the formation of metal ores. The existence of impermeable formations near the surface, could preserve the heat in magmatic rock formations.

Sedimentary formations can offer heat due to several processes. In some locations with crustal thinning basement heat flux is higher. Moreover, faults are also acting as pathways for heat movement. Sedimentary formations like shales, can prevent heat transport, which was created during the formation and upward movement of hydrocarbons and aqueous fluids.

Nonetheless of rock types, there are two types of geothermal reservoirs, which are favorable for assessment, hydrothermal that contain mineralized and/or meteoric water and petrothermal, which are referring to hot dry rock with natural or induced fracture systems, permitting fluid circulation for heat transfer. Finally, low, and medium enthalpy sources can be feasible.




## 1.6 Geothermal systems – Geothermal Reservoirs

A geothermal system is an area where the Earth's thermal energy is sufficiently concentrated to create an exploitable energy source. Geothermal systems are classified according to their geological, hydrological, and thermal characteristics [119].

<b>Low-temperature (LT)</b> systems with reservoir temperature at 1 km depth below 150°C. Often characterized by hot or boiling springs.	<b>Low-enthalpy</b> geothermal systems with reservoir fluid enthalpies less than 800 kJ/kg, corresponding to temperatures less than about 190°C.	<b>Liquid-dominated</b> geothermal reservoirs with the water temperature at, or below, the boiling point at the prevailing pressure and the water phase controls the pressure in the reservoir. Some steam may be present.
<b>Medium-temperature (MT)</b> systems with reservoir temperature at 1 km depth between 150- 200°C.		<b>Two-phase</b> geothermal reservoirs where steam and water co-exist and the temperature and pressure follow the boiling point curve.
<b>High-temperature (HT)</b> systems with reservoir temperature at 1 km depth above 200°C. Characterized by fumaroles, steam vents, mud pools and highly altered ground.	<b>High-enthalpy</b> geothermal systems with reservoir fluid enthalpies greater than 800 kJ/kg.	<b>Vapour-dominated</b> geothermal systems where temperature is at, or above, the boiling point at the prevailing pressure and the steam phase controls the pressure in the reservoir. Some liquid water may be present.

Table 2: Classifications of geothermal systems on the basis of temperature, enthalpy and physical state (Bodvarsson, 1964; Axelsson and Gunnlaugsson, 2000) [102]



Clastics		
Various		
Shale	<u>Seal</u>	Heat, pressure, and fluid barrier Interbedded shales
Sandstone	<u>Reservoirs</u>	<u>Hydrocarbon and Hydrothermal</u> Fluids Good Porosity / Permeability Conductive / Convective
Shale	<u>Source</u>	Good Total Organic Content Expulsion of Migrating Fluids
Various	e.g., Limestone	Marine, shallow shelf, lagoon Thermally conductive
Basement	Basal / Igneous / Metamorphic Rocks	<u>Heat sources</u> : Crustal Thinning (Failed Rift Valley structures), Granitoids, or Magmatic Structures

Figure 7: Characteristics of different geological formations [115].



Based on Geological setting, there are different types of Geothermal Reservoirs [115] :

- **Tectonic Plate Boundary systems**

The vicinity of plate boundaries is considered as an ideal and very promising area for Geothermal Energy exploration. The Earth's crust consists of tectonic plates which have been moving for hundreds of millions of years. There are three types of tectonic plate boundaries: convergent, divergent and transform.

At convergent boundaries, the subduction of one plate, under the other, causes its' melting. This melting is responsible for the presence of significant amounts of fluids which increase volcanic activity and they are associated with heat energy. At divergent boundaries, the two plates are spreading apart, creating new crust, leading to higher volcanic energy.

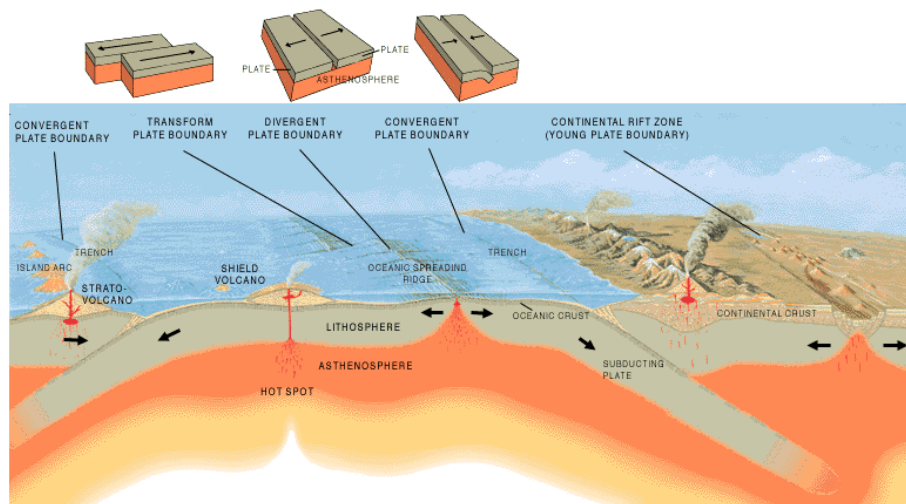


Figure 8: Types of tectonic plate boundaries (usgs.gov)

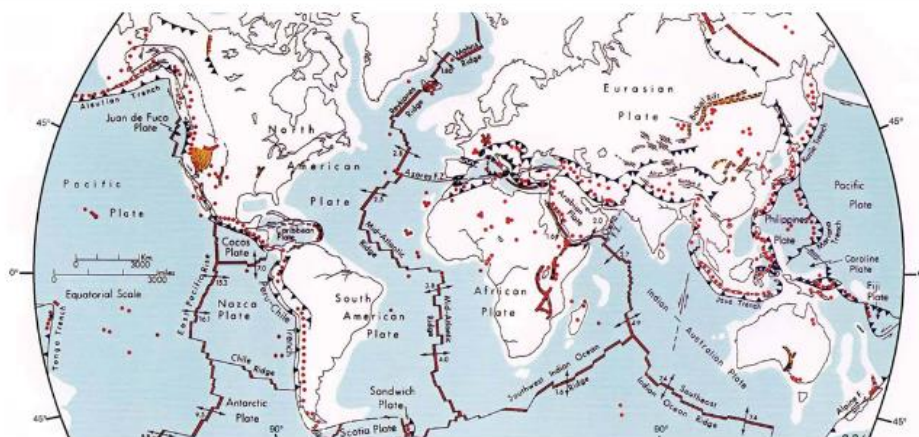


Figure 9: Tectonic plate boundaries [115]

In the Atlantic and Pacific Oceans, as well as adjacent onshore areas, all types of plate boundaries are present, with the form of volcanic island arcs and volcanic arcs (onshore).

These volcanoes could be either active or extinct with accessible heat at specific depths. The presence of hot spots (e.g. Hawaii) or thinner crustal areas is visible in the middle of some plates, where the upward movement of mantle is increasing heat energy flow.

Many locations around the globe have been already used for Geothermal Energy developments (California, Iceland, Italy, Turkey, Indonesia, Philippines, and New Zealand etc.), but thousands of locations remain to be exploited.

### ▪ Sedimentary Hydrothermal Reservoirs / Stratigraphic Geothermal Reservoirs

Hydrothermal reservoirs can be found in sedimentary rock and fractured hard rock. This type of Reservoirs has good porosity, permeability, and geothermal gradient. Probably these formations will have heated aquifers below since they were primarily used in hydrocarbon exploration and development. Heat flux is dependent on crustal thickness and basement temperature. Heat conduction is achieved through conductive rock formations and heat advection due to fluids moving upwards. These reservoirs could be exploited using repurposed, new production and injection wells, with the aim of capturing the heat for Geothermal energy from surface Binary Power Plant [115].

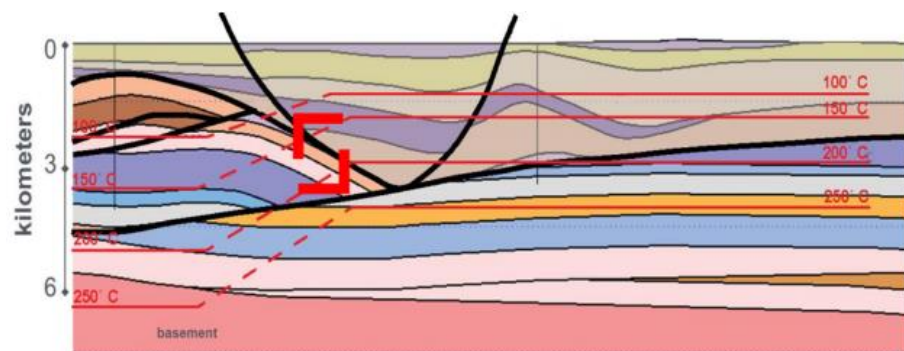


Figure 10: Geological section showing the increase of geothermal temperature with the depth (geothermal gradient) [115].

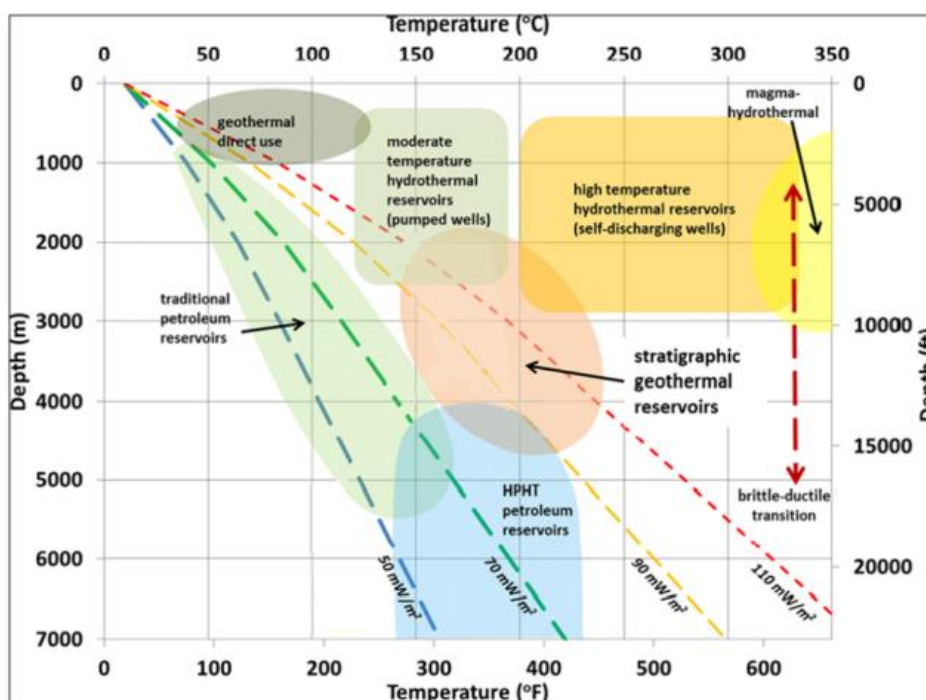


Figure 11: Temperature and depth of reservoir types (Ref. Modified from DE-EE0005128 Final Technical Report, DOE EERE – Geothermal Technologies Program, Sept 2016) [115].

- **Hard Rock Hydrothermal or Petrothermal Reservoirs in Subduction Zone Geology [115]:**

Subduction Zones are associated with volcanic, magmatic, or intrusive rock systems, that can work as heated hydrothermal or fractured hot dry rock reservoirs and have the ability to circulate fluids through the reservoirs. The released fluids contain carbon components from organic matter, carbonates, water and hydrous materials and they are moving upwards into the deep hydrothermal reservoirs. Magmatism leads to upwelling melted slab rock, which adds heat to the formations towards the surface, into petrothermal reservoirs (fractured hot dry rock).

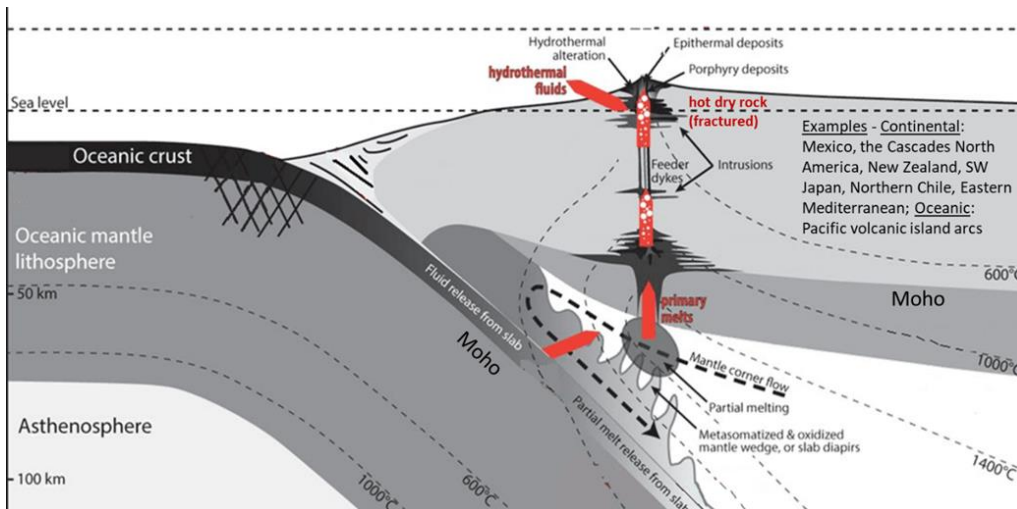
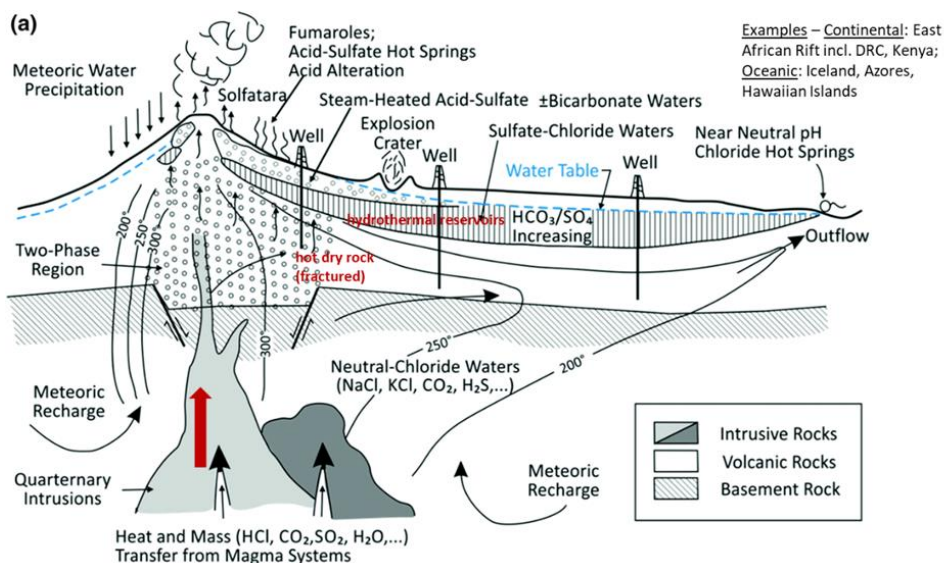


Figure 12: Illustration of Hard Rock Hydrothermal or Petrothermal Reservoirs in Subduction Zone Geology [115]

- **Hard Rock Hydrothermal or Petrothermal Reservoirs in Divergent or Hot Spot Zone Geology [115]:**

Divergent or Hot Spot Zones are associated with volcanic or magmatic rock systems, that can work either as heated hydrothermal reservoirs or fractured hot dry rock, which have the ability to circulate fluids through the reservoirs. The released fluids contain carbon components and water, and they are moving upwards into the deep hydrothermal



reservoirs. Magmatism leads to upwelling melted slab rock, which adds heat to the formations towards the surface, into petrothermal reservoirs (fractured hot dry rock).

Figure 13: Illustration of Hard Rock Hydrothermal or Petrothermal Reservoirs in Divergent or Hot Spot Zone Geology [115].



In Hard Rock Hydrothermal or Petrothermal Reservoirs in Subduction Zone and Divergent or Hot Spot Zone Geology, Surface heat flux depends on Moho temperature, magma temperature, crustal thickness, and magma ponding levels. Heat conduction is achieved through conductive rock formations and heat advection due to fluids and melts moving upwards. These reservoirs could be exploited using production and injection wells, with the aim of capturing the heat for Geothermal energy from surface Binary Power Plant [115].

## 1.7 Geothermal Exploration

### 1.7.1 Geological survey

Geology is important through all the steps of a geothermal project, especially when combined with geochemical, geophysical and engineering studies [27]. A geological survey includes the identification of a geothermal field and its characteristics, geological interpretation of surrounding formations, lithostratigraphic sequence, age, and thickness of these formations [130]. Furthermore, it is used for the identification of tectonic processes prevailing, faults, fractured rocks and permeable formations [119]. A very important stage in

geothermal exploration is the assessment of hydraulic permeability [119]. In geothermal systems permeability appears to be structurally controlled. Furthermore, faults and fractures work as fluid pathways [110]. All the techniques in table 3, are used during the exploration and development of a geothermal system.

Technique	Information obtained	Purpose
Satellite imagery	Locations of possible faults and surface manifestations;	Determine areas for geologic mapping; locate areas of potential geohazards (eg, unstable slopes, debris flows)
Geologic mapping	Types and locations of surficial manifestations, rock types, locations of faults	Identify potential reservoir lithologies, caprocks, and aquicludes; develop a preliminary conceptual model of system and initial drill targets; provide input into civil works
Petrography	Rock type, alteration mineralogy, relative ages of secondary minerals, distribution of fractures and porosity	Develop geologic history, locate zones of upflow and recharge, assess permeability distributions
X-ray diffraction	Determine rock mineralogy and percentage of primary and secondary minerals	Identify minerals that cannot be characterized petrographically (eg, mixed layer clays, zeolites); assess degree of alteration, chemistry, and temperature of the geothermal fluids, assist in developing well casing programs
Fluid inclusion analyses	Homogenization temperature, apparent salinities and the presence of daughter minerals	Characterize temperatures and compositions of fluids that have circulated through the system; assess fluid processes (boiling, mixing, conductive cooling)
Electron microprobe, SEM-EDS analyses	Mineral compositions and textures	Identification and compositions of individual minerals; mineral paragenesis and textural data
Radiometric dating	Age of rocks and hot spring deposits	Evidence of young heat sources

*Table 3: Geologic techniques frequently used during exploration and development of a geothermal system [27]*

### **The role of Petrology [27]:**

Petrology is extremely essential during a geothermal project. Petrology can provide the subsurface lithology of the cap rocks and reservoir, that is needed to determine the geological structure of the geothermal system from multiple wells and to proceed to wireline logs. Furthermore, it can provide the characteristics of reservoir formations, the geothermometry and the isotherms, the fluid flow, discharge and recharge zones and location point of heat sources.

During exploration, petrology provides information about nature, age and history of surface rocks, and the existence of hydrothermal discharge zones. At drilling stage, petrology is used for identification of rock protolith, detection of hydrothermal alteration and possible production zones and casing depths. Throughout production phase, petrology contributes to the evaluation of ejecta and wellbore scales and making decision about inject fluid composition.

Temperature, pressure, rock type, permeability, fluid composition and duration of hydrothermal activity, are the factors responsible for hydrothermal alteration and therefore for affecting the minerals and the physical properties of the rocks. Reactions between water and rocks, can either permeability and porosity increase or reduction by mineral deposition or dissolution, relatively. Thus, affecting thermal and hydraulic stresses, leading to faulting and fracturing.

### **3D Geological Mapping [110]:**

In geothermal systems, geologic structure serves an essential role in fluid flow control. In fact, the more complex the structure (e.g. intersecting and closed space faults), the more geothermal systems are hosted. 3D geologic mapping is a new technology and can be used for permeability and fluid flow assessment of geothermal systems.

3D geologic mapping includes:

- detailed geologic map
- 2D interpretive geologic cross sections
- 2D seismic reflection data
- potential field geophysical data and modelling
- downhole lithologic data interpreted from well cuttings and/or core

Geologic mapping includes rock type, structure and hydrothermal alteration, but also surface geothermal occurrences. Moreover, it includes lithostratigraphic characteristics of the field. Critically stressed faults and structural discontinuities usually related with relatively high density fracture networks and seem to be considerable fluid flow conduits. Also, lithologies that host fault zones, play a crucial role in fracture permeability. With the aim of having a sufficient interpretation of the structural and stratigraphic framework near the geothermal field, a 1:24,000 scale or higher resolution is needed. In this way, declination of faults, stratigraphy and structures, geothermal deposits and alteration data, are presented in detail.

Downhole data from boreholes provide structural and stratigraphic constraints at depth. While, Geophysical data include 2D seismic reflection data (e.g. fault structure) and provide basin shape, topographic and structural relief, fault location and structure, and strata dip direction. All these data above are limited at deeper levels, due to the limitations of seismic reflection. So, in this case gravity or magnetic data are used to interpret faults, and modelling those data together with density properties of each lithological unit, lead to structure and stratigraphy constrains. Moreover, magnetotelluric data and other types of relative electrical resistivity/ conductivity measurements can be incorporated with the rest geological data. Values of high conductivity might originate from fluid circulation and intense smectite clay alteration, which indicates the presence of "clay cap", which is common in geothermal reservoirs.

2D geologic cross sections are essential for geothermal field structure interpretation and require seismic reflection and geophysical data, downhole data and geologic map data. 3D geologic mapping is the combination of all the data mentioned above and can present the geothermal potential in 3D.

For geothermal upwelling potential evaluation using the 3D map area, the usage of data including spatial correspondence between the fracture permeability potential, elevated temperatures, and geothermal fluids, are necessary.

### **1.7.2 Volcanological survey** [130]

If the potential field is in existing near volcanic formations and regions with volcanic activity, it requires specific assessment. The characteristics and properties of this field, that are very important are, the volume of the chambers, the temperature and the depth. The analysis of hydrothermal degradation and the formation of new hydrothermal minerals, provide information about the existence and properties of the cap rock. Finally, the products of volcanic eruption must be assessed to identify the products of magma-water interactions, if the water was surface or deep origin, the fluid temperature, the age of eruption and if the thermal or hydrothermal conditions remained the same.

### **1.7.3 Geochemical survey**

The analysis of geothermal fluids and their hydrothermal effects on surface or shallow geological formations, contributes in the assessment of the geothermal situation of the potential field [113]. The analysis of samples from hot and cold surface water, springs, and steam can provide valuable information on geothermal system characteristics at a fairly low cost. Among the most important of these is the estimation of surface temperatures without expensive drilling [119]. Geo-chemical methods provide information about the type of system (e.g. steam or liquid), the origin of the fluids, the geological and mineralogical environment of the system, and possible problems in the exploitation process (e.g. sealing or erosion of pipes) [119].



#### **1.7.4 Hydrogeological- Hydrothermal survey** [130]

Geothermal fluids are found in large quantities inside the rocks, faults, in pores and even in the mineral's structure. Underground water circulation depends on the hydrogeological structure of the potential area. The alteration of meteoric waters or surface water is dependent on the type and lithology of the formations, but also on the tectonic conditions. The horizontal movement is affected from the sediments and their type. The upward movement is facilitated through faults or specific structures, such as intrusions, anticlines, etc. The quantity of the geothermal fluids is mainly dependent on hydrological conditions. The water viscosity reduces with increasing temperature, hydraulic permeability increases with temperature, while the intrinsic permeability is constant for each rock.

The quantity of underground water is affected by the structure of the pathways and the physicochemical conditions of geothermal fluids. Hydrothermal alteration can significantly reduce the permeability and storage capacity of the formations (e.g., pyroclastic). However, sometimes (anhydrite, limestones etc.) it can lead to cavities and karsts, facilitating the circulation and storage of geothermal fluids and the formation of high-quality geothermal reservoirs.

#### **1.7.5 Geophysical survey**

- **Temperature and heat flow measurements** [119]

Geothermal fields are characterized by a surface heat flux of a multiple of the average global value of 63mW/m<sup>2</sup>. The measurement of temperature and heat flow is an essential step of any geothermal research project and provides information and indications of the extent of the geothermal system and its thermal potential.

- **Magnetic Methods**

Magnetic methods are based on the detection of rock magnetization in the surface by measuring small-scale magnetic anomalies, meaning local variations in the intensity of the geomagnetic field [130]. Aeromagnetic surveys are used to identify anomalies of hot zones by mapping the Curie isotherm surface. The Curie surface reflects the depths at which ferromagnetic minerals transition to paramagnetic minerals due to the exceeding of their associated Curie temperature - isotherm. So, in areas of increased heat flux, the Curie isotherm will rise and be located closer to the surface, and in some cases, it may even be very shallow. Therefore, estimating the depth of the Curie surface is an additional technique for detecting hot zones. Magnetic methods can also be used to detect areas or phenomena of hydrothermal alteration, which also alter the magnetic susceptibility of rocks. These phenomena are expected to be associated with negative magnetic anomalies [119].

- **Gravimetric Methods**

Gravimetric methods provide identification of geological structures and characteristics suitable to act as geothermal reservoirs and pathways for the circulation of geothermal fluids [119]. They contribute, not only on exploration/exploration stage of geothermal energy, but also to the development and exploitation of geothermal resources [119].

Gravimetric methods observe variations in the earth's gravitational field, by measuring the gravity acceleration [130]. It contributes to tectonic structure identification, and characteristics [130]. The tectonic characteristics of the bedrock revealed by the interpretation of the Bouguer anomaly, are important in a geothermal field assessment since they provide information about geothermal fluid circulation and thermal conditions [130].

- **Geo-electric methods**

Geo-electric methods are used to identify the electrical properties of surface formations of Earth's crust. They calculate the distribution of specific electrical resistance of the surface layers. Geophysical survey, is used in geothermal field exploration, because low resistivity areas might be linked to underground formations with high temperature and salinity, so probably to geothermal reservoirs. Interpretation of electrical resistivity of geological formations and of water in their pores and fractures, can provide the location and way of circulation of the geothermal fluids [130].

- **Seismic methods**

The main seismic methods are seismic reflection and seismic refraction. The purpose of these methods is to determine the variations of the propagation velocities of elastic seismic waves in the surface layers of the earth's crust by measuring their travel times [130]. With the aim of revealing the spatial orientation (position, direction, inclination) of active faults, reservoir and geothermal fluid circulation paths [119]. These methods can identify the tectonic structures, that could potentially have geothermic interest [130].

According to Kasahara J. et. al., 2021 [63], the exploration of geothermal fields has been conducted with many methods, with the most direct been drilling, by obtaining core samples and/or cutting chips, but it is considered very costly. Cheaper methods are Magnetotellurics (MT) and gravity ones, which are conducted at the surface or the air. Nevertheless, they do not provide high location accuracy and depth resolution required for geothermal reservoirs. In oil and gas exploration, seismic methods are the most reliable, however in the case of geothermal fields are not really applicable, because they are mostly located in highly heterogenous geological structures, which attenuate the seismic waves from the source. The New Energy and Industrial Technology Development Organization (NEDO), Japan, has developed a project that promotes supercritical water utilization geothermal power generation. Another promising approach method for geothermal field exploration, is the use of optical fiber for seismic measurement -distributed acoustic sensing (DAS) and many times combined with distributed temperature sensing (DTS) and full waveform inversion (FWI).

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## 1.8 Companies

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There are many companies around the world that are involved with Geothermal Energy resources and exploitation of them. Some of them are presented below.

- **PETROLERN inc.** [88,89]

PETROLERN is a company that deals with leading-edge clean energy technologies, to sustain safe and optimized carbon storage, geothermal and Oil & Gas operations. PETROLERN is using the pre-existing knowledge from Oil & Gas sector, towards clean energy, with the aim of reducing Oil & Gas industry footprint. Currently, it develops innovative and cost effective technologies to make geothermal energy operations economic viable and profitable. Concerning geothermal sector, PETROLERN has been dealing with subsurface thermal energy storage (Synthetic Geothermal batteries), geothermal systems and power plant designing, reservoir stimulation, design, and modelling of EGS.

Nowadays, PETROLERN is in partnership with the University of Utah, to broaden experimental research capabilities and gain access in Utah FORGE underground field, in Milford, with the aim of testing and developing technologies for EGS.

- **Stellae Energy** [112]

Stellae Energy is a company based in UK, which provides end to end green and clean energy solutions. Latterly, they are engaging extensive technical projects throughout the globe, in partnership with large energy groups and multilateral organizations, to identify sustainable energy locations, sources, solutions.

- **Baseload Capital** [8]

Baseload Capital has established power companies, aiming in power plant development and operation, in Iceland, Japan, Taiwan, USA and New Zealand. Baseload Capital is engaged with low temperature heat without drilling to extraordinary depths and waste management from existing power plants.

- **Rock Energy** [99]

Rock Energy provides complete heating systems, which use the geothermal heat of the subsurface, with the aim of using eternal clean energy. Rock Energy has come up with solutions to overcome problems regarding installation space, that can be significantly reduced. Their energy wells are expected be a leading application in the heat and power market. Deep energy wells have a depth of 2-3km and require less space on the surface and can provide 30 times more energy than shallow ones.

- **GET Group** [44]

Rock Energy offers renewable and sustainable, emission-free energy by using deep geothermal wells. It is applied and is operational at Oslo Airport Gardermoen ('OSL') more than three years. Lightcircle of Norway, is a manufacturer of cutting-edge technology that improves energy efficiency, safety, and expands into technologies for smart homes.

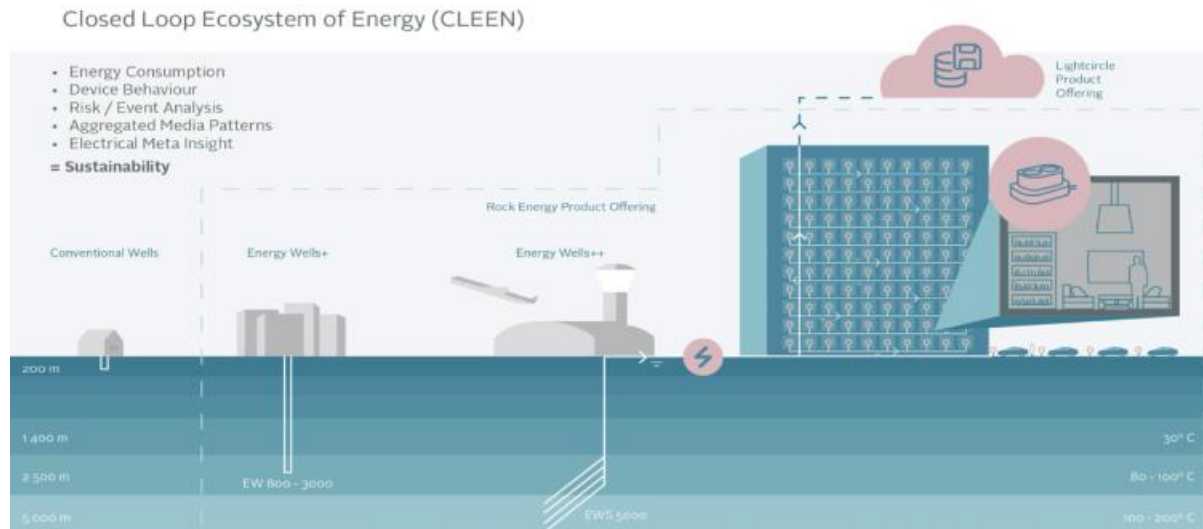


Figure 14: Synergies between Rock Energy & Lightcircle – Closed loop Ecosystem of Energy [44]

- **Steps Energy** [116]

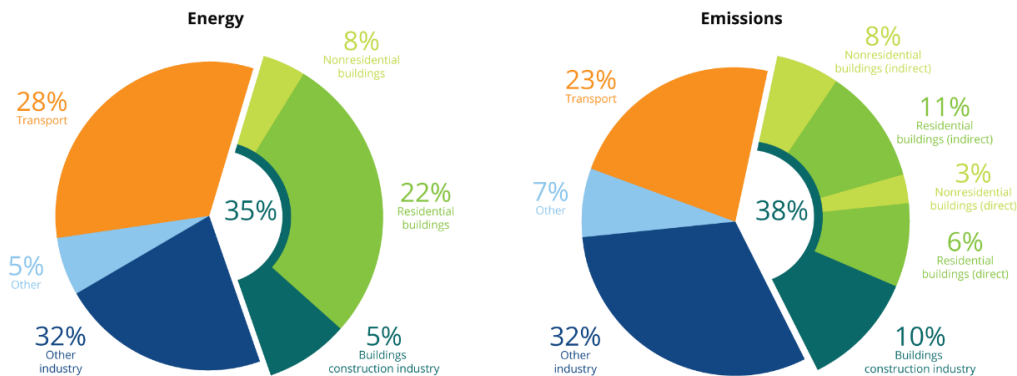
Steps Energy would like to expand in Saudi Arabia and raise the awareness of un-utilized geothermal resources. This production plan for geothermal base load resources, it is hoped that it will be implemented till 2030. Steps Energy offers end-to-end Geothermal consulting services, to facilitate discovering new geothermal opportunities that are profitable, and develop them safely.

- **Schlumberger** [104,105]



Figure 15: Schlumberger's print worldwide in the Geothermal Sector [105]

Schlumberger has been operating in the subsurface since 1922 and it is present in geothermal fields or more than 50 countries and it participates on 70% of global geothermal projects. GeothermEx exists from 1973 and its acquisition from Schlumberger took place in 2010. Taking into account all the above, Schlumberger seems to be the most ideal and well equipped company for geothermal energy operations. Geothermal power has reached 8,000 MW, leading to more than USD 14 billion in geothermal project financing. Schlumberger has the experience and technologies required for EGS developments, since it has been dealing with tight shale projects for decades.



Global share of buildings and construction final energy and emissions, 2019. (Sources: IEA 2020d; IEA 2020b. Adapted from "IEA World Energy Statistics and Balances" and "Energy Technology Perspectives.")

Figure 16: Global share of buildings and construction final energy and emissions, 2019. (Sources: IEA 2020d; IEA 2020d. Adapted from "IEA World Energy Statistics and Balances" and "Energy Technology Perspectives" [105].

Schlumberger New Energy, provide the necessary technical consultancy and cutting-edge business models that optimize the value of geothermal resources and the power they produce, achieving that way a cost-effective geothermal development and improved success rates in geothermal power ventures.

The Schlumberger New Energy (Celsius Energy) uses geothermal energy for heating and cooling operations and Schlumberger's knowledge and technologies throughout the years, led to reduced emissions by using Celsius Energy solutions worldwide.

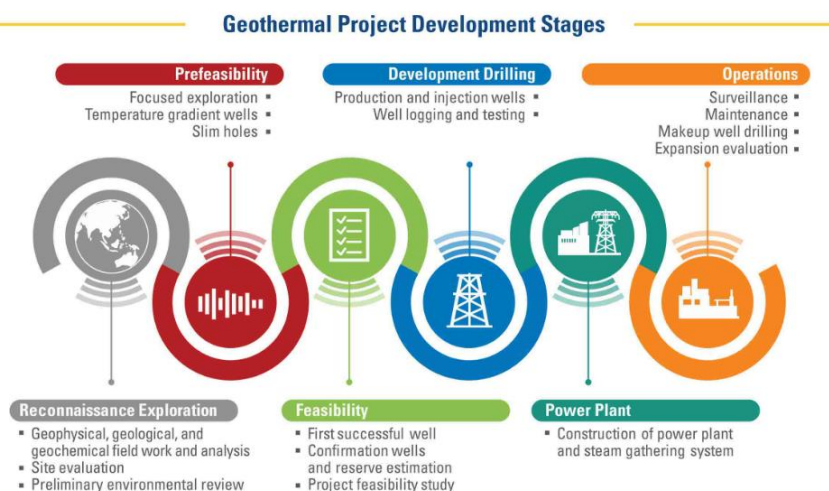


Figure 17: Geothermal Project Development Stages [105].

The Celsius Energy is an innovative technology includes:

- ✓ geoenery exchanger: reduces footprint at surface, increases real estate value and provide viable solutions for new building constructions or existing building renovation projects
- ✓ surface heat pump: allows energy transportantion from subsurface to the buildings for heating, cooling purposes
- ✓ advanced digital control: monitoring and controlling in real time of the above, reducing maintenance demands, and providing efficiency reports.

▪ **GeTech** [45]

Getech Group, is a Geoenery & Green Hydrogen Company, which uses its world-leading geoscience data and unique geospatial software products, for geoenery and green hydrogen projects exploitation, development and operation.

GeTech developed or has been using a variety of tools to identify potential geothermal fields such as:

- Heat seeker: assess attractive geothermal locations
- Depth to basement: Quantify sediment fill and basin extents.
- Exploration analyst: Geothermal play assessment made easy
- G&M services: Survey planning, QC, advanced processing and integrated geophysics interpretation
- G&M training: Understand how to use G&M data as essential components in an integrated geoscience project
- GIS services: Business intelligence and spatial analysis for enhanced decision making.
- Gravity Data: A cost-effective component of your integrated exploration program for anywhere in the world
- Magnetic Data: Map depth to basement, structural lineaments, Curie isotherm and volcanics to help de-risk interpretation uncertainties.

Especially Heat seeker is a very important tool in geothermal field assessment and provide maps of geothermal suitability. It considers, temperature at depth, surface heat flow & temperature, tectonism, structure, infrastructure & transportation and socio-economic market.



- **Eden Geothermal** [25]

Eden Geothermal Ltd has been established by Eden Project, EGS Energy Ltd, and Bestec (UK) Ltd to proceed with the deep geothermal energy field in the granite beneath Cornwall.

Eden Geothermal Cornwall [77] project funding is reaching £16.8 million (£9.9m from the European Regional Development Fund, £1.4m from Cornwall Council and £5.5m from institutional investors), and it concerns the drilling of a 4.5km deep well at the Eden Project, and heat its famous Biomes, greenhouses and offices [25]. After this step, which is phase one, phase two will start with drilling of another 4.5km well and manufacturing of an electricity plant [25].

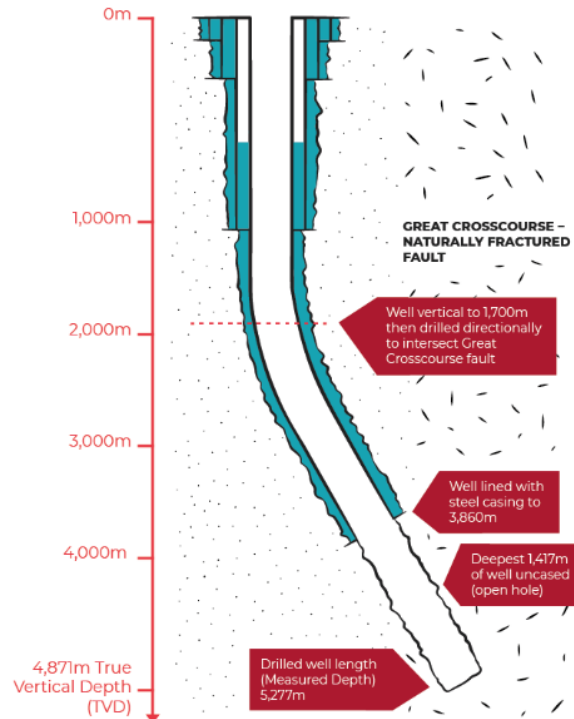


Figure 18: Illustration of geothermal well developed in Eden Geothermal Cornwall project [25]

- **Europa Oil & Gas, UK, Ireland and Morocco**, are attempting to assess the potential of West Firsby, as a sustainable, clean geothermal energy system. If this project is successful, it is believed that will be capable of extracting and using this heat throughout Europe. West Firsby field is located in the East Midlands. It is in late productive life, composed of nine pre-existing wellbores with seven wellheads. The wellbores cover a 2.5 km<sup>2</sup> area and reach a depth of 1,680 m. All the parameters above, together with the accessibility of data collected over the last 34 years and the geothermal gradient, make West Firsby one of the best and promising locations in the UK, with geothermal resources [121].

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## 1.9 Future

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Geothermal activity is expected to rapidly increase in the future, more specifically if government targets worldwide are to be met, \$3 billion threshold are estimated in 2026 [41]. Rystad Energy's geothermal dashboard includes over 1,700 geothermal power generation and direct use projects worldwide. According to this dashboard, the drilling activity has been increased between 2015 and 2020 (1,100 geothermal wells for power generation – approximately 180/ year). Considering the growth of geothermal energy usage, 500 wells per year are anticipated in 2025 [41].

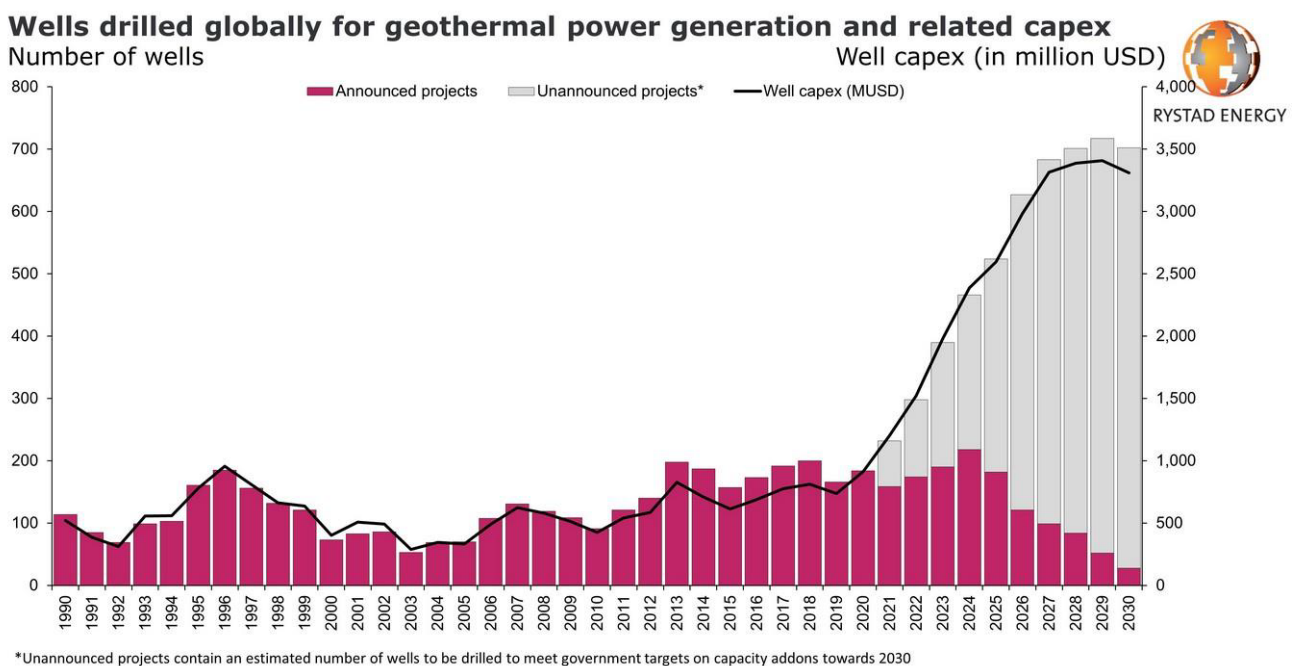


Figure 19: Rystad Energy Geothermal Analysis Dashboard [41]

Geothermal industries are governed by high-enthalpy regions, that necessitate the drilling of 2-3km wells. Reservoirs having temperatures more than 200°C are used for power generation. These requirements affect the well location factor, since high-temperature reservoirs located at 2,000 meters or below are quite limited. To remedy this and increase geothermal accessibility, new technologies like EGS (Enhanced Geothermal Systems) and AGS (Advanced Geothermal Systems) are being developed. The major markets for geothermal district heating and power generation, are Europe and China [41].

Geothermal technology is proven safer than Hydrogen or CCS, of which the costs are in the same range, but it has a long way to prove its progress. Even though Geothermal resources have a lot of advantages such as, available 24/7, well understood and proven technology, already used for decades for heating and power generation, the main objectives are to scale up, proceed deeper and become worldwide. As mentioned above, the way to achieve that is by developing EGS and AGS projects. These projects will increase large-scale geothermal projects near big demand centers. Drilling operation is a very costly procedure, but once the drilling is finished, the well can provide heat for decades [34].

As Flower, S. et. al., 2021 [34] mentions, based on many experimental projects, the levelised cost of electricity (LCOE) of AGS/EGS projects in 2021 was US\$180/MWh. It is expected that government support, technology innovations and an influx of investment, will dramatically reduce the costs. More specifically, costs of US\$75/MWh by 2030 and US\$55/MWh by 2050 are achievable. Furthermore, it is believed that a competitive LCOE will be game-changing and the potential of geothermal capacity could reach, even exceed, 1,000 GW by 2050, which is higher value than either global nuclear or hydro capacity.

### Cost reductions could make geothermal competitive by the early 2030s

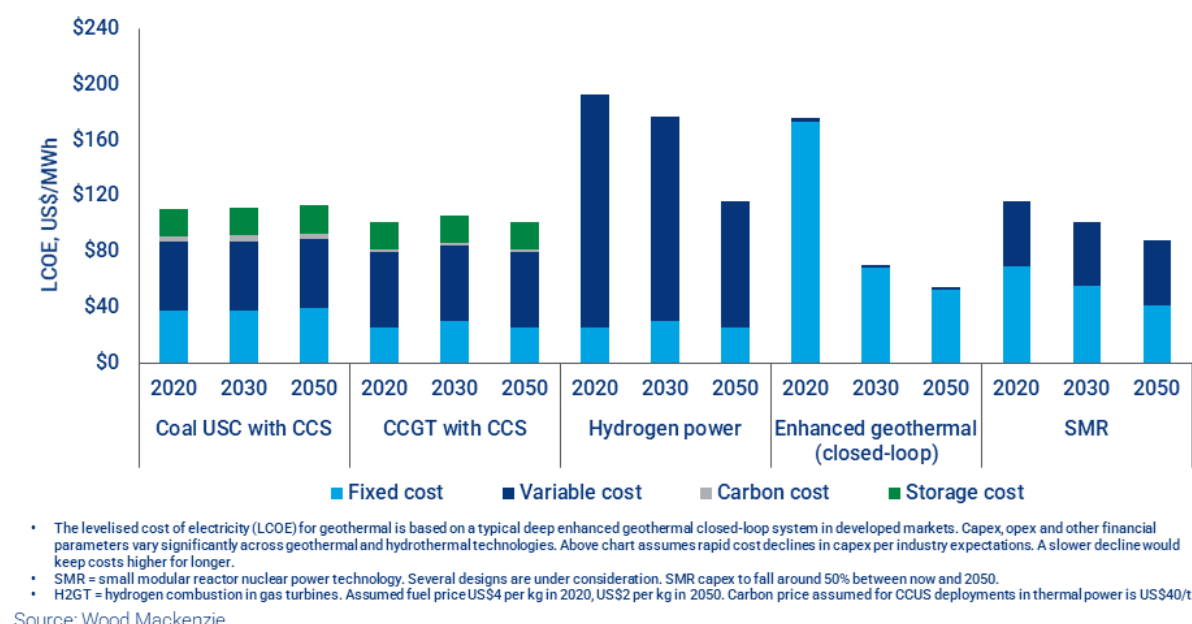


Figure 20: Cost reductions in different projects for power generation [34].

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### 1.10 Greece

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Greece presents a very complex geological structure with a wide variety of geological formations, because of its complex geological history and evolution. Geotectonically, belongs to the southern edge of the Euroasiatic plate, which has been fragmented due to the subduction of the African plate, under the European plate, in South Aegean [4]. Greece presents high and intense tectonic and magmatic/volcanic activity [4,83], with a heat flow

reaching more than  $80 \text{ mW/m}^2$  [4]. This heat flow is derived from the formation of the South Aegean Active Volcanic Arc, and it is responsible for the development of high temperature geothermal reservoirs [83], such as Milos and Nisyros islands [4].

Lower temperature geothermal fields are associated with grabens, observed in the Central Aegean and post-orogenic sedimentary molassic basins observed in the southern boundaries of the Rhodope and Servo-Macedonian Massifs [4].

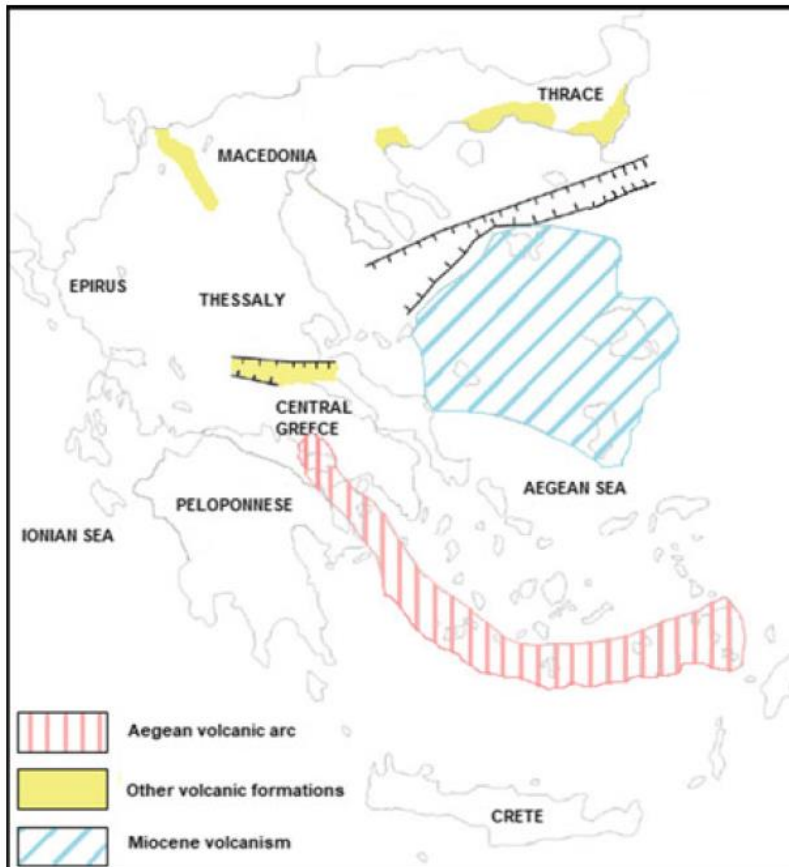


Figure 21: Main geotectonic structures in Greece [4].

The geothermal fields of Greece are located in [83]:

- Eastern Macedonia and Thrace (Sedimentary Tertiary Basins: Evros Delta, Xanthi, Nestos Delta, Strymon) due to the presence of permeable rock formations, extensive tectonic activity, faults, magmatic intrusions and crustal thinning.
- Central Macedonia, is characterized by extensive and deep NW-SE active faults, which lead to low temperature geothermal fields (Langadas and Nea Apollonia-Mygdonia Basin).
- Central Greece (Sperchios, Euboea island, Thermopylae, Edipsos) presents a high heat flow, with reservoirs existing in Cretaceous limestones, due to the effect of North Anatolian Fault.
- East and Northeast Aegean islands (Samothrace, Lesvos, Chios and Ikaria) are governed by low to medium temperature geothermal reservoirs, associated with Miocene volcanic and tectonic activity.

- Western Greece (Ionian islands, Peloponnese, Crete and the south Dodekanese islands) is not considered favorable for geothermal exploration, with low heat flow, as a result of geotectonic position (Hellenic Trough and Sedimentary arc)



Figure 22: Main Geothermal areas of Greece [83]

Geological setting of Greece has contributed to the formation of a substantial number of geothermal fields with high geothermal energy potential, with 55 to have already been identified. Geological setting in Greece, is heterogeneous, so different conditions are prevailing into each region. This is the reason, why the geothermal fields are dispersedly distributed. The temperatures vary from 25 to 90 °C, mainly in depths <500m, with a potential of 1,000 MWth [4,50]. The majority of geothermal fields is located in Macedonia, Thrace and the Aegean Islands [4].





Exception to the rule are more than 5 of the geothermal fields, whose temperatures range from 90 to 125 °C, while two fields present temperature higher than 150 °C and are entitled as the most important high temperature deep geothermal systems in Greece, one in Milos Island at 325 °C and one in Nisyros Island at 400 °C [4].

Even though there are perennial studies and many geothermal fields were discovered, utilization seems limited, and only applied for direct uses [50]. Local communities and authorities are against large-scale exploitations, meaning the ones with temperatures over 90°C. On the contrary, low temperature (25-90°C) deep geothermal utilization is perceived much more positively. Many steps must be taken, in order to cultivate awareness and accurate informing towards high temperature deep geothermal exploitation [50].



Main reasons for the delay of geothermal resources in Greece [50]:

- lack of an adequate
- regulatory framework and bureaucratic barriers
- lack of financial capital
- lack of investment incentives
- lack of infrastructure
- lack of strategic planning for rational exploitation of geothermal energy

A zero-pollution technology is under development. In this closed-loop system, the geothermal fluid after being used, will be reintroduced into the subsoil, thus ensuring zero gas emissions. This technology will also ensure uninterrupted power supply on the island of Nisyros, to resolve issues with potable water through desalination and apply district heating of homes and greenhouses [50].

IGME, NKUA and other universities have made a research regarding the risks of exploitation in Nisyros. IGME stated that the exploitation of the geothermal field, installation, and operation of a geothermal power plant in Nisyros, will not oppose any risks, regarding physicochemical imbalances such as to cause any volcanic reactivation [50,95]. But there is a lower risk of hydrothermal explosions, which have already formed more than 20 craters in Lakki area [95]. Nonetheless, this exploitation could be profitable, since the causes of explosions are linked with hydrothermal fluids having intense pressures due to circulation and seismic activity [95]. NKUA also stated that there will not be a negative impact on the above processes, instead it will be beneficial, because it contributes to the depletion of volcanic energy [50,95].

Geothermal development and advancement of technology, changes in policy promotion and regulations, will contribute in significantly reducing negative environmental and health impacts and encountering problems faced in the past. These steps will probably have a positive impact on the society, leading to more open-minded opinions about high-temperature geothermal exploration [50].

PPC Renewables proposed a 5MW power plant design and installation, in a remote location [50], but it is not willing to proceed without the consent of the majority of the local community [95].

Under the partnership with Helector SA, Terna Energy and Terna Aioliki Xerovouniou SA, PPCR long-term plans about development and installation of 4 Power Plants, in leased geothermal fields include [18,85,96]:

- Milos-Kimolos-Polyegos islands group, with capacity of at least 5MW
- Nisyros island, with capacity of at least 5MW
- Lesbos island, with capacity of at least 8MW
- Methana peninsula (in mainland), with capacity of at least 5MW

### **Geothermal exploration activities from 2015-2019:** [83]

- **Lesvos island:** 30-33°C, at 150m
- **Lemnos island:** 24-29.6°C, at 70-105m
- **Euboea island (Edipsos):** 30-82°C
- **Eastern Thessaly:** 35.1-41.3°C, at 235-410m
- **Santorini island:** 26-27°C, at 40-190m
- **Strymon basin (Macedonia, Northern Greece):**
  - 1) Sidirokastro: 75°C, at 100-300m
  - 2) Lithotopos-Iraklia: 37.5-74.5 °C, at 353-520m
  - 3) Nigrita: 61°C, at 216m
- **Strymonikos Gulf (Macedonia, Northern Greece):** 46 °C at 130m, 85 °C at 230m, 90 °C at 515m
- **Nestos Delta Basin (Macedonia, Northern Greece):**
  - 1) Eratino-Chrysoupolis: 70-80°C at 600-700m, 150-180 °C at 1500-1800m
  - 2) Neo Erasmio-Magana: 30-68 °C, at 150-500m
- **Evros Delta Basin (Thrace, Northeastern Greece):** 89-99 °C at 200-400m

### **On-going Geothermal activities:** [83]

- **Geothermal Power Production Project:** PPCR and HELECTOR S.A. collaboration, mentioned above.
- **Geothermal field of Aristino:** The Municipality of Alexandroupolis [1,83] invested €6 million for the development of a geothermal project, with the aim of manufacturing a district heating system and heat distribution for agricultural purposes [83]. This geothermal field has a range of temperatures between 30-99 °C [97].
- **Geothermal field of Nea Kessani:** 'AGRITEX Energy" invested (T<sub>max</sub>=82°C), with the purpose of heating a 5 ha hydroponic greenhouse for cluster tomatoes, which will reach 10 ha, leading to a total investment of €10 million.

- **Geothermal field of Akropotamos [8]:** The Municipality of Paggaio invested in a low temperature geothermal field, the amount of €10 million, with the aim of developing district heating/cooling network and distributing heat to semi-urban settlements, greenhouses and spa resorts. This project is still at early stages.
- **Geothermal field of Lithotopos:** The Municipality of Iraklia has been exploring a low temperature geothermal field.
- **Geothermal field of Nymfopetra (Mygdonia Basin, Macedonia):** This field will be used for agricultural purposes, by drilling three new exploration boreholes and rehabilitate two pre-existing productive geothermal wells. Electrical resistivity tomography has revealed a very low resistivity anomaly, which is most likely connected to a geothermal resource, at a depth of less than 250 meters.

## 2. Carbon Capture Sequestration (CCS)

Carbon Capture and Storage strategies have been manufactured in order to prevent carbon dioxide ( $\text{CO}_2$ ) from releasing into the atmosphere and mitigate global warming, that is responsible for climate change [22]. The main way to achieve that, is by injecting the  $\text{CO}_2$  into geologic formations with high permeability that form deep structural reservoirs [133]. The foremost geological targets for  $\text{CO}_2$  storage are, depleted oil and gas fields, deep saline aquifers and deep unminable coal seams [81,133] and basalt formations [2]. The permeable and porous geological strata used for storage must be overlain by an impermeable formation in order to seal the reservoir [22].

Carbon dioxide emissions will be captured from natural sources and human sources [2]. Natural ways of releasing  $\text{CO}_2$  are ocean release, decomposition, and respiration etc. On the other hand, human sources emitting  $\text{CO}_2$ , in the atmosphere, from coal-based power plants and oil and gas sector, but also from industries producing chemicals, fertilizers, cement, even mining [2]. Then compressed in similar pressure and temperature that we come across below 1 km depth, to achieve a fluid state, which is easier to transport through pipelines. In that form, we can store larger amounts of  $\text{CO}_2$  by injecting into deep geological formations permanently.

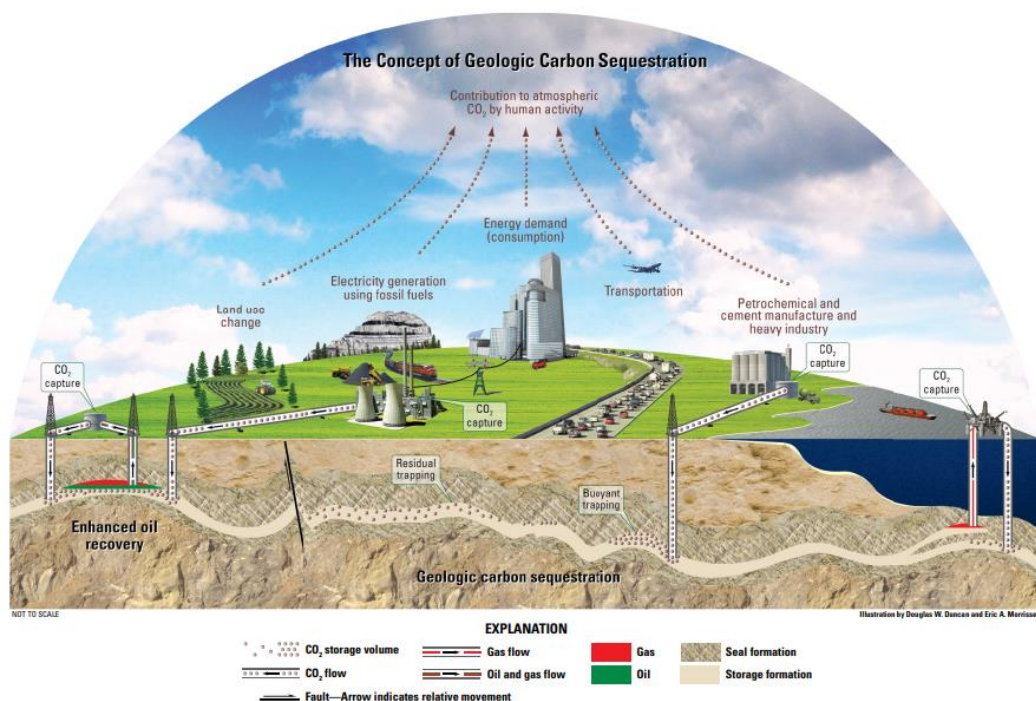


Figure 24: The concept of geologic carbon sequestration. Figure composed by Douglas W. Duncan and illustrated by Eric A. Morrissey.(Duncan & Morrissey, 2011)

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## 2.1 Capture

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**Geochemistry** techniques play the first role in capturing the CO<sub>2</sub>. There are three technologies of capturing CO<sub>2</sub>, based on the amount of CO<sub>2</sub> in the gas stream, the pressure, and the type of fuel [5,21,58]:

- Industrial process capture systems
- Post-combustion capture: separation of CO<sub>2</sub> from the flue gas
- Pre-combustion capture: CO<sub>2</sub> separation in the fuel mixture
- Oxyfuel: combustion under pure oxygen conditions

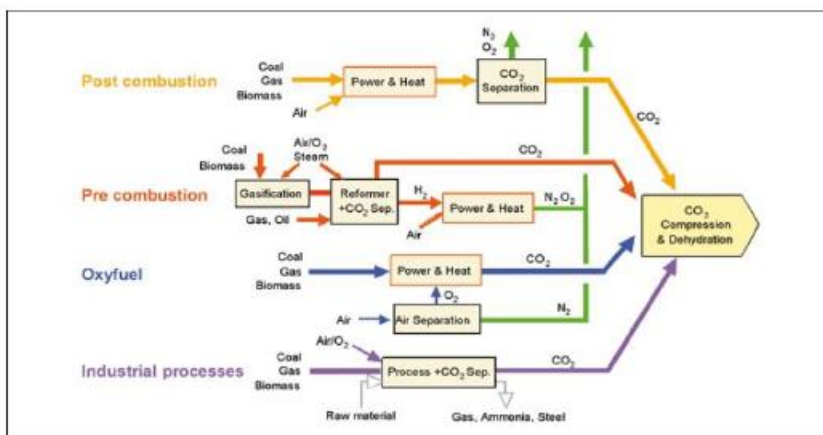


Figure 25: Capture methods (source BP) [5,58]

- **Industrial process capture systems** [5,58]

Carbon dioxide has been captured by industrial process streams for 80 years, but most of it was released to the atmosphere because storage processes wasn't developed. A typical example of this method is the purification of natural gas and the production of a synthesis gas containing hydrogen (used in ammonia, alcohol, and synthetic liquid fuel production). On the contrary, cement-steel industry and fermentation processes for food and beverage production, even though they produce CO<sub>2</sub> they don't contribute to capture. But this CO<sub>2</sub> could be captured with post-combustion, oxy-fuel combustion, or pre-combustion techniques.

### 1. Natural gas sweetening

Natural gas sweetening is the removal of H<sub>2</sub>S and CO<sub>2</sub> and depending on the volume of CO<sub>2</sub> in the gas, it uses chemical solvents, natural solvents, or membranes to achieve separation. The specifications of most pipelines, require CO<sub>2</sub> <2%, to avoid corrosion and minimize energy costs for transportation. Usually, natural gas sweetening uses various alkano-amines. However, when there is high concentration of CO<sub>2</sub>, the use of membrane systems is more economic viable. Membranes offer lower cost, lower energy consumption, applicability in remote areas (e.g., marine areas) and flexibility.



## **2. Iron and steel industry**

The iron and steel industry are the sectors that consumes the most energy worldwide. Nowadays, direct reduced iron-DRI which is called sponge iron due to its shape, is used to increase iron quality. The production of sponge iron requires the reaction of an oxygen-rich iron ore with  $H_2$  and  $CO$ , whose products are reduced iron,  $H_2O$  and  $CO_2$ . Therefore, sponge iron production processes might capture pure  $CO_2$ .

## **3. Cement production**

The cement production industry occupies the 6% of  $CO_2$  emissions from stationary sources. Cement production processes emit gases that contain 15-30%  $CO_2$  by volume, but it is not captured. Although, the capture is probably possible by post-combustion with additional steam production to regenerate the solvent, oxy-fuel combustion, or the use of calcium sorbents since it is in excess.

## **4. Ammonia production**

$CO_2$  is the by-product of ammonia production ( $NH_3$ ), in which  $CO$  and  $H_2O$  is converted into  $CO_2$  and  $H_2$ , then the  $CO_2$  is removed and transformed into methane (extraction of  $CO$  and  $CO_2$ ), to create the ammonia. Only a part of the produced  $CO_2$  is available for storage, since ammonia production industry are combined with urea production industry, which exploit the 70-90% the produced  $CO_2$ .

### **▪ Post-combustion**

The post-combustion capture is the capture of  $CO_2$  from the gases that are produced during the combustion of fossil fuels and biomass [5,58,11]. Most of  $CO_2$  is separated, then transported and stored in an underground reservoir, without affecting the environment [5,58].

$CO_2$  is a small fraction of the exhaust emissions of a power plant, so the direct storage of the entire volume of exhaust gases ( $CO_2$ , Nitrogen Oxygen and Water vapors) is unfeasible due to the insufficient storage space and the requirement of significant amount of energy to compress them. Therefore, the methods that are used, capture only the  $CO_2$  [21]. Carbon dioxide can be extracted from the natural gases by using liquid and stable sorbent absorption, membrane segmentation and cryogenic distillation [2].

This application has a very important advantage, because it permits us to modify older power plants by implementing a "filter" that captures  $CO_2$  during its passage through chimneys [31]. This filter is a  $CO_2$  absorbent solvent, which if we heat it, water vapor will escape, resulting a concentrated stream of  $CO_2$  [31]. The low  $CO_2$  concentration has two disadvantages, the first the first one is the necessity of large and expensive equipment to treat large volumes of gas and the second one is the necessary usage of strong solvents to capture and release the  $CO_2$  [21]. One technique to separate  $CO_2$  from gases mixtures is by adding an amine solution. After mixing, the amine is heated to release pure  $CO_2$  and returns to be reused [21].

Post-combustion technology has been tested on small scales providing CO<sub>2</sub> recovery at a rate of up to 800 tons/day. However, the major challenge is testing and performance at large scale [67].

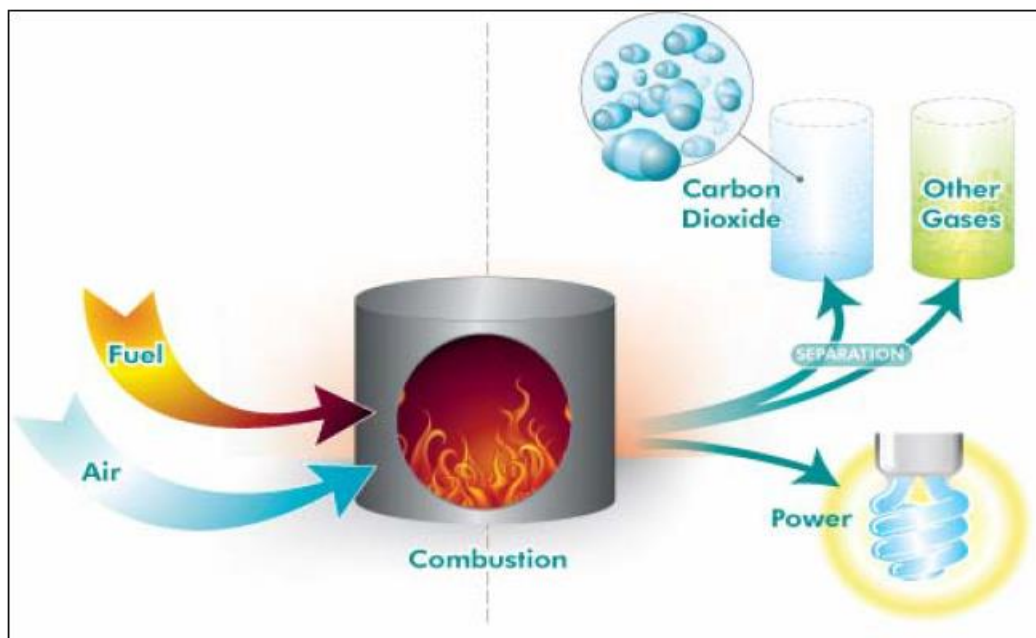


Figure 26: Post-combustion capture process (source: <http://www.co2crc.com.au>)

CO<sub>2</sub> capture in Greece is achieved with separation from gas mixtures, that are produced in large industrial processing facilities, such as coal-fired power plants (e.g., Kozani station, Ptolemaida) and natural gas (e.g., Elpedison), steel mills, cement plants (e.g., TITAN) and refineries (e.g., MOTOR OIL) [16,23].

## Technologies for CO<sub>2</sub> capture

### 1. Membranes

Membranes are made by materials that allow gas to flow through them. They are mainly composed polymers, ceramics [5,21,58] and metallics. The flow also depends on the pressure difference within the membrane. Thus, when using membranes for separation, high pressure flow is preferred [5,58]. Membranes allow to a specific component of the gas mixture to pass faster than the rest [21]. Some of the membrane types are porous inorganic membranes, palladium membranes, polymer membranes and zeolites membranes [21]. This technology cannot offer high separation degree, so it requires multiple stages and recycling, which increase the cost and difficulty [21]. Although membranes are commercially used, their reliability and economic viability for CO<sub>2</sub> capture is not sure yet [5,58].

Membranes can separate (gas separation membranes) and capture the CO<sub>2</sub> within a solvent (gas absorption membranes) [21].

### ✓ **Gas absorption membranes [21]**

Membrane is used together with a solvent to capture CO<sub>2</sub>, which more specifically is dispersed between the pores of the membrane and absorbed by the solvent. The membrane acts as boundary between the gas and liquid phase, by taking advantage of the permeability of the pores. Absorption membranes are useful when CO<sub>2</sub> has low partial pressure (e.g., as exhaust gas), as the driving force for gas separation is small [21]. Unfortunately, in most cases the gas and liquid phase are mixed, which causes flow problems, such as fuming and streaming. These problems make the use of a membrane within the absorber essential. The use of a membrane can lead to size reduction of the equipment required to absorb the CO<sub>2</sub>. Research is being directed towards the development of suitable materials which ensure that the solvent does not penetrate the pores of the membrane [21].

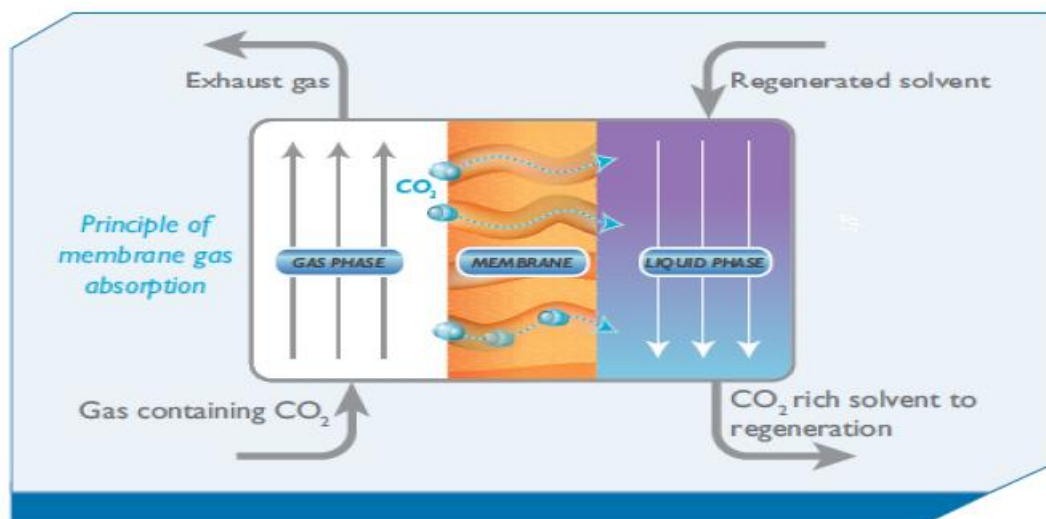


Figure 27: Capturing process of CO<sub>2</sub> with gas absorption membranes [21]

### ✓ **Gas separation membranes [21]**

In this technology, there is no need of a solvent, and the equipment is smaller. The main cost is the energy required to reach high enough pressure difference the membrane to complete the separation. These membranes act as semi-permeable barriers, so CO<sub>2</sub> passes through more easily than other gases.

The parameters responsible for the movement of a gas through the membrane are:

- The size of its molecule
- the concentration of the gas
- the pressure difference behind the membrane
- the attraction of the gas as opposed to the membrane material

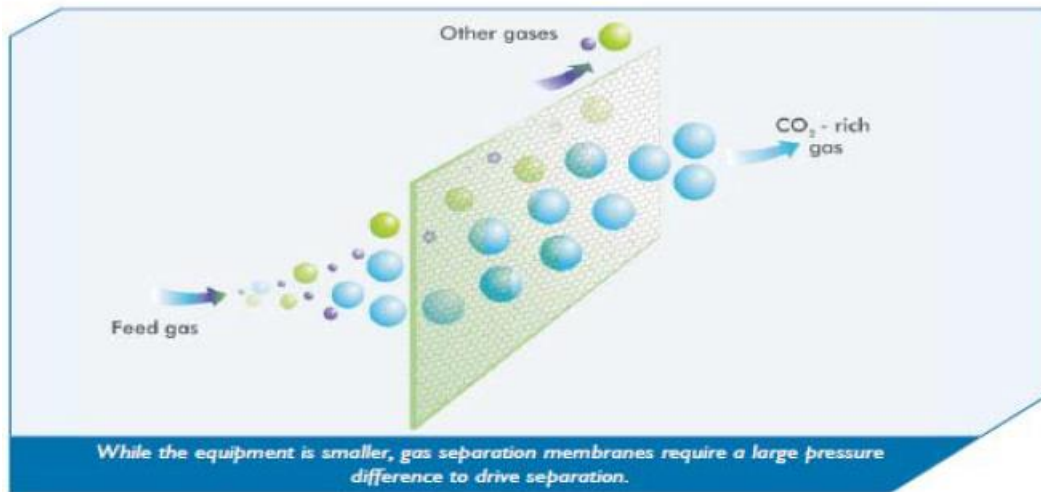


Figure 28: Capturing process of CO<sub>2</sub> with gas separation membranes [21]

## 2. Solvents

Solvent absorption is the most common process for CO<sub>2</sub> separation from exhaust gases (Nitrogen, CO<sub>2</sub>, Oxygen and Water at atmospheric pressure) and for the purification/enrichment of natural gas [21]. If the CO<sub>2</sub> is present in large quantities, their capture demands lots of repeated cycles and the use of suitable solvent, to be successful [5,58]. The gas passes through the liquid chemicals that absorb CO<sub>2</sub> and release it afterwards into another tank at higher temperature. In the absorber the gases are being partially cooled and in contact with the solvent. The solvent absorbs the CO<sub>2</sub> at 40-60°C [21]. The CO<sub>2</sub>-enriched solvent, is moved into another column (desorber), where it is heat at 120 °C, causing it to be released. CO<sub>2</sub> is cooled to remove the water, which returns to the desorber and together with the 'purified' solvent is pumped back to the absorber [21]. The reactions between the chemical solvents and the CO<sub>2</sub> can ensure the capture. To release and capture of CO<sub>2</sub> from the solvent is necessary the use of heat [21]. The common chemical solvents in this process are the amines, ammonia, and carbonates [21].

## 3. Adsorption [21]

Adsorption can be used to separate CO<sub>2</sub> from gas mixtures, more specifically with solid adsorbents, such as zeolites and activated carbon. There are two types of processes, pressure swing adsorption (PSA) and temperature swing adsorption (TSA), which are used commercially for CO<sub>2</sub> separation from natural gas. However, adsorption is not widely applicable, due to small capacity of the adsorbents, but if they are combined with another capture technique, they increase the rate of success [21].

#### 4. Cryogenic separation

CO<sub>2</sub> can be separated from other gases by cooling and condensation [21]. Gas can be transformed into liquid by compression, cooling, and expansion. The components of the liquid phase gas can be separated using the distillation column. In that way, oxygen can be separated and used in CO<sub>2</sub> capture systems (oxy-fuel combustion and pre-combustion capture), if it is available in large quantities [5,58]. More specifically it is used in high CO<sub>2</sub> concentration gases, above 90% [21]. In addition, separation by cooling can be used to separate impurities containing high levels of CO<sub>2</sub>, in oxy-fuel combustion as well as in the CO<sub>2</sub> removal from natural gas [5,58]. Cryogenic is applicable to gases with high pressure and concentration of CO<sub>2</sub>, as in the case of pre-combustion capture and combustion under pure oxygen conditions[21].

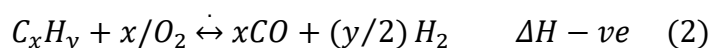
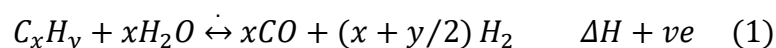
This method has some drawbacks, the cooling process demands high amount of energy and the presence of some components like water could lead to blockages during cooling, which means they should be removed before the cooling process of the gas mixture [21]. However, the advantage in this technique is the production of liquefied CO<sub>2</sub>, which is necessary for some means of transport, like trucks (tankers) or ships [21].

##### ▪ Pre-combustion

This method aims in increasing CO<sub>2</sub> concentration and partial pressure [21]. Pre combustion takes place before the completion of the combustion process and it involves [2], adding oxygen or air or steam to the fossil fuels [5,21,58] under high temperature to produce synthesis gas, which contains H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub> [2]. More specifically, it requires the reaction of the fuel with oxygen and/or steam to produce mainly CO and H<sub>2</sub> [5,21,58]

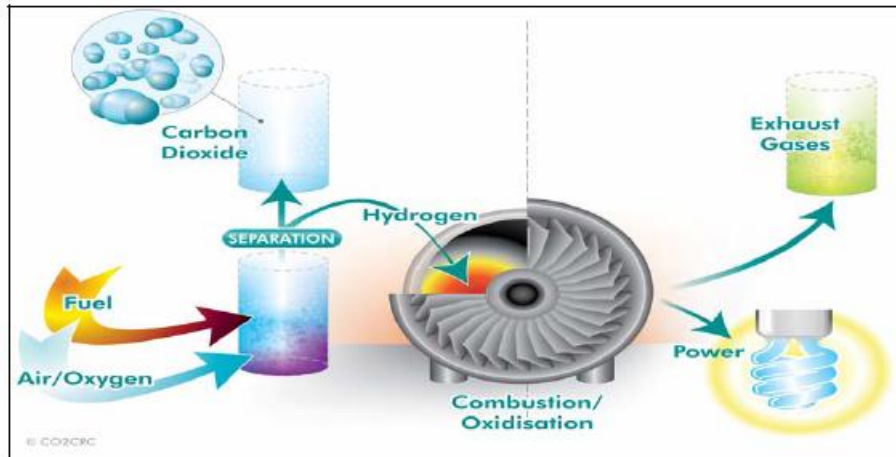
Additionally, CO reacts with the steam in a catalytic reactor/ converter and produces more H<sub>2</sub> and CO<sub>2</sub> [21], which leads to higher concentration of CO<sub>2</sub>. The CO<sub>2</sub> is then separated and the H<sub>2</sub> is used as fuel in a mixed cycle gas turbine [21]. So, carbon dioxide can be captured, by converting the fuel into hydrogen [81]. The high CO<sub>2</sub> concentration (> 20%) in the H<sub>2</sub>/CO<sub>2</sub> fuel gas mixture enables the separation of CO<sub>2</sub> [67].

The main reactions are either the addition to the fuel of steam - 'steam reforming' (1) or oxygen (2), which is called 'partial oxidation' when applied to liquid and gaseous fuels, and 'gasification' when applied to solid fuels [5,58]



The CO<sub>2</sub> produced is then separated with physical or chemical adsorption process, and creates a hydrogen-rich fuel, that has many applications. The captured CO<sub>2</sub> can be transported for storage [5,58].



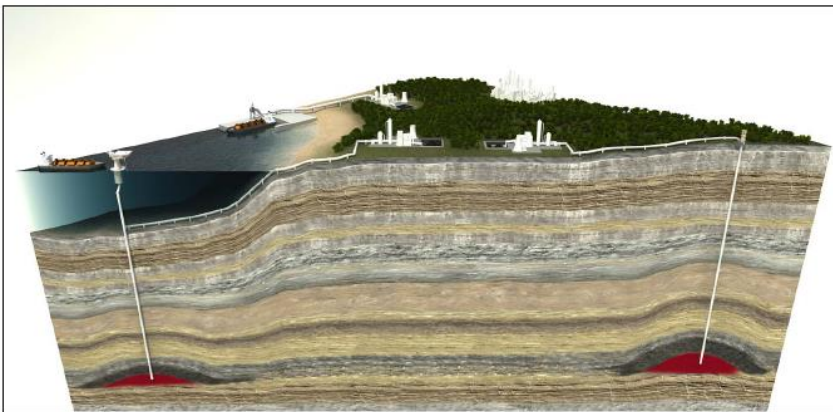


# Geology and Geochemistry

the primary role, in CO<sub>2</sub> transportation. In terms of Geology, geological

characteristics and properties, sub-surface formations, faults and fractures, affect transportation process. On the other hand, in terms of Geochemistry, chemical reactions (e.g., pipeline corrosion) and impurities, can complicate CO<sub>2</sub> transport process.

CO<sub>2</sub> transportation is one of the most important steps in CCS, since it “connects” the geological reservoirs with the industrial facilities [2]. So, basically transport links source with storage sites [58]. After capture, CO<sub>2</sub> is separated, then compressed and transported [16,21,23] in gaseous, liquid, and solid form, by tankers, pipelines, and ships as long as the



CO<sub>2</sub> is in gaseous or liquid form [5,58,59], or other methods to a suitable geological storage site. Transport processes must follow the regulatory framework regarding public safety, including pipelines and shipping [58].

Figure 30: Methods of transporting captured CO<sub>2</sub>, by tankers, subsea pipelines and terrestrial pipelines (source: <http://www.bellona.org/imagearchive/ProsjektlabTransport.png>) [21]

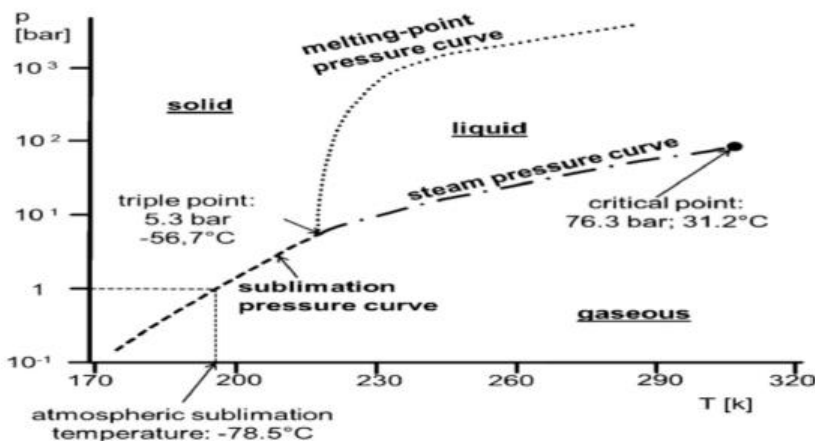


Figure 31: Phase diagram of pure CO<sub>2</sub> [35,59]

Efficient CO<sub>2</sub> transport requires the gas density to be equivalent to its liquid phase. CO<sub>2</sub> must be in a supercritical state, which occurs at a pressure of 1070 psi (76,3 bar) and a temperature of 31,1°C (88 °F). CO<sub>2</sub> is evaporated under ambient pressure at a temperature of -78,5 °C (194,5 K) [59].

CO<sub>2</sub> is considered to be an inert and easy manageable gas, which is already being transported by high-pressure pipelines [21]. So, if CO<sub>2</sub> was transported at pressures close to atmospheric, it would occupy large volume which necessitates very large facilities to process it [5,58,59]. But if it is compressed then it occupies less volume and can be transported by pipeline. This volume can be reduced by compression and transportation of the gas through suitable pipelines [58,59], under high pressure [5]. So, the most economical way of CO<sub>2</sub> transport is the pipelines [21].

However, the volume can be further reduced by i) liquefaction, by well-established technology in LPG (liquefied petroleum gas), LNG (liquefied natural gas) and transportation of liquid CO<sub>2</sub>, ii) solidification (high energy consumption and costly method) or iii) hydration. [5,58,59]. A new technology is considered to replace the LNG, and someday to be used in CO<sub>2</sub> transportation [5,58]. If CO<sub>2</sub> sequestration becomes widespread, there will be need of pipeline networks, to improve ease of management and provide larger economic profits. Nowadays, there isn't yet transport by ships, that will be used for long distances, but tankers, like ones that transport LPG, will be implemented soon [21].

Transport methods are dependent on economics as well as geographical criteria. A highly potential future transport option is related to transportation to the nearest storage point [59].

### **2.2.1 Pipeline transportation**

Pipelines can transport CO<sub>2</sub> in a liquid or gas form. In new infrastructures, liquid form is preferable, because it has higher density and provides higher flow rate. But gas form is preferable, when the reuse of an existing natural gas infrastructure that reaches the "end of its life" is needed [2].

Currently the transportation of CO<sub>2</sub> in large quantities is achieved by pipeline, mainly for enhanced oil recovery (EOR) [58,59]. Pipelines can be installed in deserts, mountain ranges, agricultural areas, heavily populated areas, farmland and the open range, in the Arctic and sub-Arctic, as well as seas and oceans with a total depth of 2200 meters [58,59]. Pipeline transportation depend on geographic conditions, safety issues and the storage location [59,107].

The transport of small amounts of CO<sub>2</sub> is a well-established technology, which can carry up to a few Mt/year [58]. On a global scale, CO<sub>2</sub> transport pipelines can reach up to 5600 km with a diameter of up to 0.762 m and carry 50 Mt/year [5].

A corrosion-resistant alloy (stainless steel) is used in some parts of the pipelines [58] and then CO<sub>2</sub> is dried to reduce the possibility of pipeline corrosion, which are made from steel (carbon-manganese steels) [5,58]. Corrosion rates are much higher if free water is present [58]. In general CO<sub>2</sub> doesn't consider as an explosive gas, however when CO<sub>2</sub> is transported in a gaseous state, it is denser than air, so at high concentrations or lowland areas, risk is increased [5]. Since CO<sub>2</sub> is transported in a supercritical state and it is 10

times denser than methane, and the average distance between stations has a range of 200 km and 120-160 km respectively, CO<sub>2</sub> transport will require less energy [5].

The presence of impurities such as H<sub>2</sub>S or SO<sub>2</sub> can increase the risk associated with possible pipeline leakage, which can cause damages, corrosion, or failure of pipeline valves. Monitoring is essential to reduce the risks associated with possible pipeline corrosion [5].

The development of an adequate network of transport pipelines is considered essential for the short-term success of CCS technology [5]. More specifically, according to studies, a CO<sub>2</sub> transport network in Europe, could demand approximately 30,000 to 150,000 km of pipelines, depending on the characteristics of the subsurface [5]. Leakage in pipeline system is relatively unlikely, but to minimize the risk in case of an accident, the pipeline network should build away from heavily populated areas [21].

### **2.2.2 Ship transportation**

Ships combine capture and storage [2]. CO<sub>2</sub> transport by ship offers flexibility in terms of the delivery time of CO<sub>2</sub> for storage and it allows the capture and combination of CO<sub>2</sub> from different sources (small to medium size) and reduces the cost of infrastructure investments [5]. Even though the capital investment is lower in this case, the shipping cost is much higher [2].

Ships are used for CO<sub>2</sub> transportation in large volumes and present common characteristics with LPG or LNG transport [59]. The properties of CO<sub>2</sub> such as pressure, volume, and temperature allow it to be transported either by semi-refrigerated tankers (at -50 °C and 7 bars) or by LNG carriers [5]. Ships have same technology to semi-refrigerated tankers, whose capacity range from 10000 to 40000 m [59].

The transport of CO<sub>2</sub> by ship offers flexibility, as they can transport different volume gases from different sources. So, the transport costs are decreasing. This transport method offers faster delivery times [59,107]. Modern technology focuses on transport vessels with a capacity of 10-50 kt [5].

### **2.2.3 Quality criteria and CO<sub>2</sub> purity in transport**

According to Ioannis Ilias, 2020 [59], CO<sub>2</sub> is captured together with various other gases (H<sub>2</sub>S, SO<sub>2</sub>), referred to as impurities. The captured CO<sub>2</sub> is then purified and compressed to be transported. Purification of CO<sub>2</sub> can cause problems in storage capacity, injectability as well as corrosion in the pipelines, which can be minimized using special monitoring devices. CO<sub>2</sub> transportation and storage must comply with certain purity regulations to avoid risks.

The European Union CCS Guideline states that CO<sub>2</sub> storage requires the gas mixture to be composed mainly of CO<sub>2</sub> and the concentration of impurities must not affect the integrity of the storage facility or the transport infrastructure. The composition of the purified exhaust gas depends both on the power plant fuel and the capture process used.

CCS technology line	Component	Coal (vol%)	Natural gas (vol%)
Post-combustion	SO <sub>2</sub>	<0.01	<0.01
	NO <sub>x</sub>	<0.01	<0.01
	N <sub>2</sub> /Ar/O <sub>2</sub>	0.01	0.01
Pre-combustion	H <sub>2</sub> S	0.01–0.6	<0.01
	H <sub>2</sub>	0.8–2.0	1
	CO	0.03–0.4	0.04
	CH <sub>4</sub>	0.01	2
Oxyfuel	SO <sub>2</sub>	0.5	<0.01
	NO <sub>x</sub>	0.01	<0.01
	N <sub>2</sub> /Ar/O <sub>2</sub>	3.7	4.1

Table 4: Typical impurities, distributed according to the capture method and the burning fuel

Each CO<sub>2</sub> pipeline operator establish the minimum specifications for gaseous mixture composition. For pipeline integrity, CO<sub>2</sub> purity must be at least 95%. In addition, low nitrogen concentration is important for EOR, but not so important for storage [58,59]. A CO<sub>2</sub> transportation pipeline through populated areas might have a lower specified maximum H<sub>2</sub>S content for safety reasons [58,59].

Component	Concentration	Criterion
CO <sub>2</sub>	>95%	Mixability
N <sub>2</sub>	<4%	Mixability
C <sub>m</sub> H <sub>n</sub>	<5%	Mixability
H <sub>2</sub> O	<480 mg m <sup>-3</sup>	Corrosion
O <sub>2</sub>	<10 ppm	Corrosion
H <sub>2</sub> S	<10–200 ppm	Safety
Glycol	<0.04 ppmv	Operation
Temperature	<50 °C	Material

Table 5: CO<sub>2</sub> concentration limits

#### **2.2.4 CO<sub>2</sub> transport risks**

According to Ioannis Ilias, 2020 [59], CO<sub>2</sub> transportation doesn't have risk of explosion or ignition, but high concentrations can cause numerous problems. These include negative impacts on humans, fauna and flora, particularly in lowland areas.

Depending on their dimensions and lengths, pipelines can carry thousands of tons of compressed CO<sub>2</sub>. Therefore, the probability of damage to the pipeline depends on its diameter. Usually very small pipelines, less than 100mm in diameter, present higher risk. Failure is significantly reduced for pipelines of 500mm diameter and above. The possibility of pipeline damage can be reduced with cleaning techniques, continuous monitoring, and appropriate maintenance techniques [76].



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## 2.3 Storage

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**Geology** is mainly responsible for the storage of CO<sub>2</sub>. As, storage depends on geological characteristics and properties, such as type of rocks/sediments, porosity, permeability, presence of suitable caprock, and geological activity (faults and fractures). Nonetheless, **Geochemistry** has a part in storage process, due to the reactions that take place in specific formations after CO<sub>2</sub> injection. However, **Geophysics** has also a part in CO<sub>2</sub> storage, as it provides a “picture” of the subsurface.

Geological storage is considered as the most viable solution [16,23] for CO<sub>2</sub> emissions to be trapped, and reduction of global warming effects and associated climate change [67]. It takes place in a variety of geological formations in sedimentary basins, that will be mentioned below, and is possible in both, onshore and offshore sites [5].

The goal is to capture the atmospheric CO<sub>2</sub> and storage it, at least for 10 thousand years. Geological storage is possible, judging from the fact that oil and gas have been stored for millions of years, and have remain intact, without releases, through natural disasters [2].

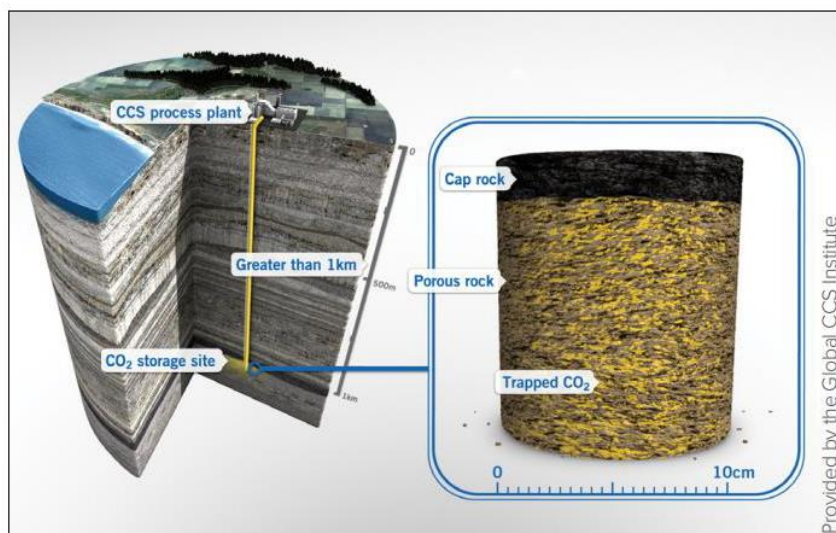
GCS technology in geological formations is considered a relatively safe solution, the structural characteristics and behavior as it is generally already known. The main concern is the possibility of leakage and the environmental impacts [59].

### Major components of a CO<sub>2</sub> storage site:

- **Reservoir rocks** must have a sufficient porosity and permeability, to store and transmit fluids. Its storage capacity is also important. Reservoir rocks are commonly composed of sandstones or carbonates [64].
- **Trap** is the 3D arrangement of rocks [2], that is responsible for not allowing the upward movement of CO<sub>2</sub> to the surface [64], but preserve is in a specific area [2]. For example, if there is a dome, CO<sub>2</sub> will rise due to buoyancy from injection point up to the center of the dome [2].
- **Cap rock/ Seal** is an impermeable layer, usually mudstones [2], that will stop the migration of CO<sub>2</sub> towards the surface. They should have the right shape to prevent, not only upward movement, but also lateral [64].

### **2.3.1 Criteria for storage site selection and parameters associated with effective geological storage sites:** [5,23,46,67]

- Enough porosity, permeability, and efficient pore connectivity to ensure easier movement
- a seal/ caprock to prevent CO<sub>2</sub> migration and permanently trap CO<sub>2</sub>
- detection of potential CO<sub>2</sub> leakage pathways to ensure safety and permanent storage
- reservoir volume: sufficient thickness and area, so enough capacity
- depth: the CO<sub>2</sub> must be stored in a supercritical state, which has characteristics of both liquid and gas, and can be compressible and have fluid-type density. Depending on the geothermal gradient prevailing in the region, the CO<sub>2</sub> density will increase rapidly with the depth, till about 800 m depth, where the injected fluid will be in a supercritical state [5]
- mineralogy: reservoirs and rocks (e.g. basalts, Volos) must contain minerals (e.g. Ca-rich mafic minerals) which can capture CO<sub>2</sub>
- stable geological environment, to maintain the integrity of the project
- small distance from source point, is preferred due to lower costs
- economic constraints



*Figure 32: Geological characteristics that ensure parameters effective CO<sub>2</sub> storage [46,47]*

The decision of the geological site depends on the depth, pressure, temperature. Since pressure increases with depth and CO<sub>2</sub> can exist as gas, liquid, or solid hydrate, it provides many options [2].

**2.3.2 Sites for CO<sub>2</sub> storage:** that can retain CO<sub>2</sub> for several hundreds of years, don't adversely affect the environment, have low costs, and comply with international regulations, are: [3,6,21,59,117]

1. Depleted oil and gas reservoirs - Enhanced Oil Recovery (EOR) and Enhanced Gas Recovery (EGR)
2. Deep saline aquifers (unused saline water- saturated reservoir rocks)
3. Deep unminable coal seams - Enhanced coal bed methane recovery (ECBM)
4. Ocean depths
5. Other suggested options (Basalts, Oil shales, cavities (caverns), abandoned mines and chemical storage)

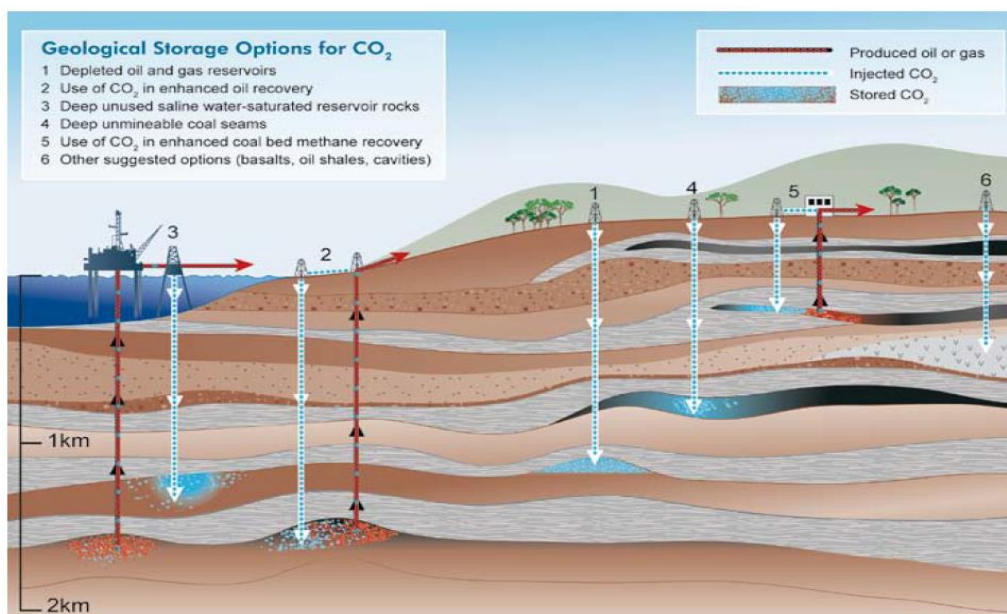


Figure 33: Options for storing CO<sub>2</sub> in deep underground geological formations (after Cook, 1999) [58]

1. **Depleted oil and gas reservoirs** are existing in permeable formations overlayed by impermeable and have syncline shape [21] and have the potential to be used as storage sites, because [3,5,21,59]:
  - they can retain CO<sub>2</sub> for several hundreds of years, as they provide integrity considering they are proven trapping locations that have effectively trapped oil and gas for millions of years
  - low costs
  - geological structure and physical properties are already known
  - enough knowledge about oil and gas storage, such as movement of fluids and their trapping mechanism
  - Infrastructure and wells already exist and can be used for CO<sub>2</sub> injection and storage processes

CO<sub>2</sub> injection and storage in depleted oil and gas reservoirs, can provide Enhanced Oil Recovery (EOR) or Enhanced Gas Recovery (EGR). Depleted gas reservoirs are a valuable storage option as there is the potential to recover up to 95% of natural gas. However, in oil reservoirs, recovery can reach up to 75%, making them less desirable [59]. On both cases on-going monitoring is necessary to avoid any leakages [59]. If considering a high price scenario, annual stored CO<sub>2</sub> will be the 1/3 of the annual oil output [2]. As

mentioned above these sites have established trapping and storage characteristics, making the process easier [46].

### Enhanced Oil Recovery (EOR)

In this process  $\text{CO}_2$  is injected in the depleted oil reservoirs and displaces the oil [5], offering high economic profits due to oil production increase [5,59]  $\text{CO}_2$  storage during enhanced oil recovery is achieved by displacing the oil and fill up the voids [3].

More specifically, from the original oil in place, 5-40% is usually recovered primarily [59,67]. An additional 10-20% can be recovered secondarily by  $\text{H}_2\text{O}$  injection [59]. Finally, using tertiary production methods, it is possible to recover 7-23% of the original oil in place [5,59]. Usually, EOR could be increased by 10-15% during  $\text{CO}_2$  injection [21]

The technologies for  $\text{CO}_2$  injection in EOR are mature and demand studies on various aspects of EOR, such as flow simulation [14,67,127] geochemical modelling [13,67,90] and leakage/risk assessment [66,67]  $\text{CO}_2$  injection is dependent on the temperature, the pressure of the storage tank and the composition of the crude oil [59,107].

In order to have a successful recovery, reservoir must be thin (less than 20 m), inclined and homogeneous. In the case the reservoir is heterogeneous, the efficiency of the storage is deeply affected. Also, Reservoir pressure is important, because it affects solubility of carbon dioxide in the oil and its recovery [59].

Gravity plays an important role in  $\text{CO}_2$  mixing with oil. Typically for oils with a gravity of 15-25 API, the mixing is mediocre, while for oils with a gravity of 25-48 API the mixing is characterized as complete [59].

Density difference between the  $\text{CO}_2$  and the oil causes the gas to move inside the reservoir. This can be worsen by the reservoir being homogeneous and having high permeability. Therefore, the heterogeneity of the reservoir is favorable, as it limits the upward movement of  $\text{CO}_2$  and forces it to move laterally, thus providing greater utilization of the formation and greater storage potential [59, 117].

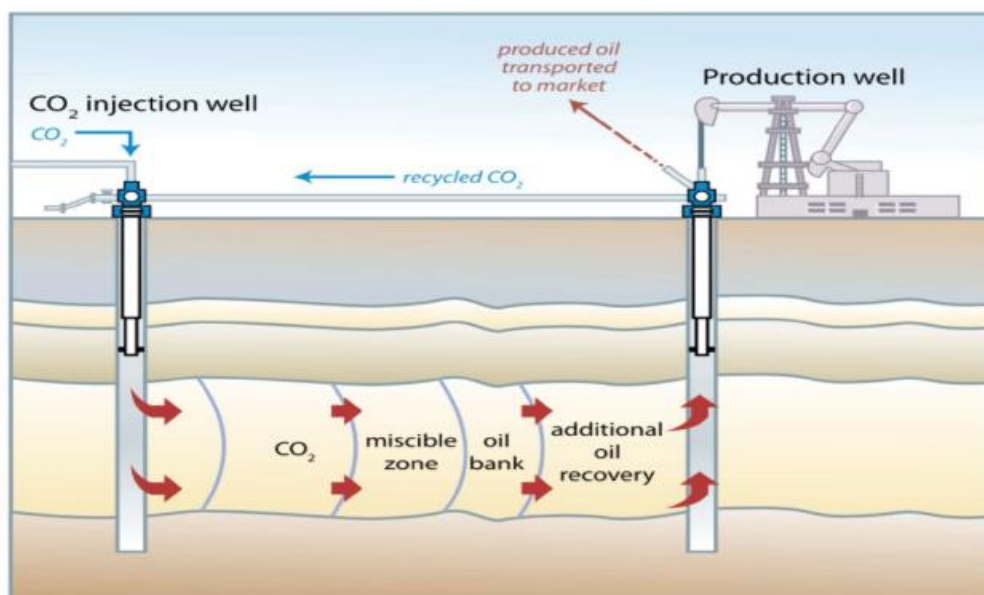


Figure 34: Enhanced Oil Recovery with  $\text{CO}_2$  injection [58,59,117]

## Enhanced Gas Recovery (EGR)

Gas recovery with CO<sub>2</sub> injection, is achieved by repressurizing the reservoir. This process has so far been implemented only at pilot scale (Gaz de France K12B project, Netherlands) [5,58].

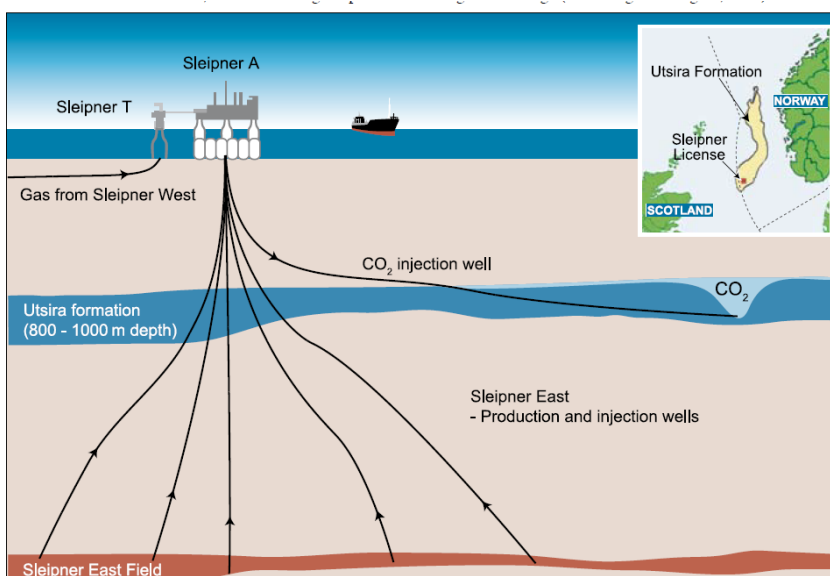
## 2. Deep Saline Aquifers

Saline aquifer formations composed of sedimentary rocks located at depths of 700-1000 m, saturated in saline water [5,67]. Deep Saline Aquifers are very common and widely distributed geographically, making them high potential sites for CO<sub>2</sub> storage [2]. They represent the highest storage capacity and the most promising environment for effective CO<sub>2</sub> storage [3,60]. These reservoirs can be found in extensive areas both onshore and offshore [52,67]. Despite the high CO<sub>2</sub> storage potential, there is relatively less knowledge compared to other geological sites such as coal deposits and oil fields [67].

The advantage is that these aquifers have no commercial value, it cannot to be used for industrial, agricultural, and human purposes [3, 67] due to salinity [5] but they can be used to store injected CO<sub>2</sub> captured by CCS [67].

The density of CO<sub>2</sub> is significantly increasing with the depth, and becomes supercritical around critical depth, which in most cases is at 800m, leading that way to smaller volume of CO<sub>2</sub> that can easier fill the reservoir pores [60]. Therefore, at depths greater than 800 m the temperature and pressure of the carbon dioxide will exceed supercritical pressure, which is desirable in terms of storage [59].

These aquifers provide high storage capacity due to the extensive presence of water, that dissolves the CO<sub>2</sub> [59], into the saline water and reacts chemically with the surrounding formations, creating metals that will trap it [21].



However, due to these enormous volumes of saline water, they are suitable for low enthalpy geothermal energy production. Thus, making these locations unsuitable for storage, as they are identified of intense geological activity, meaning intense fracturing and temperature increase with depth [5,59]. So, pressure, temperature and the integrity of the trap structure are key factors in the development of the geothermal system [59].

Figure 35: Simplified diagram of the Sleipner CO<sub>2</sub> storage Project. Inset location and extent of the Utsira formation. [58]



### 3. Deep unmineable and uncommercial coal beds

Deep unmineable and uncommercial coal beds are being used for Enhanced Coal Bed Methane Recovery (ECBM) with the injection of  $\text{CO}_2$ , that can reach 90%. in comparison with other methods than can only retrieve 50% [5,59].

After methane recovery,  $\text{CO}_2$  is stored in the formations, at shallow depths. This process is dependent on permeability of coal beds and their absorption of  $\text{CO}_2$  [3]. Coal has high permeability because it consists of fractures, that have micropores absorbing the gases [5, 59], trapping  $\text{CO}_2$  into the porous coal structure [67].

During the  $\text{CO}_2$  injection into the coal,  $\text{CO}_2$  is absorbed easier than methane [5,59], releasing in that way the methane. Coal will absorb and trap  $\text{CO}_2$  permanently, if the deposit will never be mined. As mentioned, usually the extracted methane from coal deposits is only at 50% recoverable, but  $\text{CO}_2$  injection increases the percentage of recovered methane and consequently the trapped % $\text{CO}_2$  is increased too. Coal has the ability to absorb  $\text{CO}_2$  volume about twice than methane's [21]. Nonetheless, coal beds usually cannot be utilized due to their small thickness or great depth [21].

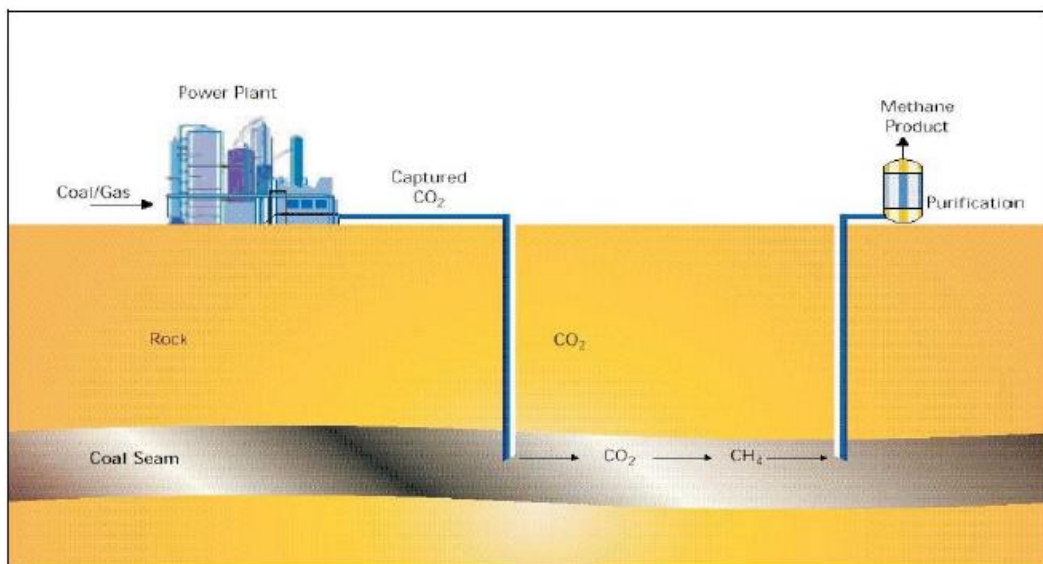


Figure 36: ECBMR technology with  $\text{CO}_2$  injection [21,55,59,73]

### 4. Ocean Depths

Injected  $\text{CO}_2$  in the oceans, results into a higher density fluid being injected into saline water, leading  $\text{CO}_2$  to remain at injection depth or to move further deeper. Therefore, it ensures its permanent storage, and its upward movement is considered impossible. Even though it is considered a viable and economic solution, there are concerns regarding the potential impacts in marine life and their environment [21].

Ocean depths are the biggest natural reservoir [67]. and represent a potential reservoir for  $\text{CO}_2$  with huge capacities, but viability of infrastructures and means of transport are still under investigation [21].

The methods that can be applied to store CO<sub>2</sub> in the oceans are:

- Injection of CO<sub>2</sub> at depths of 1000-2000m, where CO<sub>2</sub> is soluble in water [21]
- Injection of CO<sub>2</sub> on the ocean floor at depths greater than 3000m, results in CO<sub>2</sub> liquefaction and sink towards the bottom due to its higher density than water [10,54,67]. So, CO<sub>2</sub> is under pressure and mainly forms underwater static lakes [2,21,59], leading to its permanent storage for at least 1000 years [59]. Injection at depths greater than 3 km can provide permanent geological storage CO<sub>2</sub> even with large geomechanical disturbances [54,67].
- Injection of CO<sub>2</sub> at the 3000m, in locations where is deeper, so that a plume is formed, which will keep sinking due to density [21].

Oceans contain about 38000 Gt of carbon and absorb CO<sub>2</sub> from the atmosphere with a rate of 1,7 Gt/year [67]. They produce 50-100 Gt of carbon (in the form of phytoplankton) per year, which is greater than from terrestrial vegetation [67,128]. The ocean's carbon reserve is about 50 times that of the atmosphere [67,94].

However, this approach is more controversial than other methods of geological storage, because injecting large amounts of CO<sub>2</sub> directly into the oceans can affect the chemistry of seawater (such as lowering its pH) causing ocean acidification and eutrophication, which can have catastrophic consequences, such as reduction of biodiversity and extensive altering of marine ecosystems [67,108].

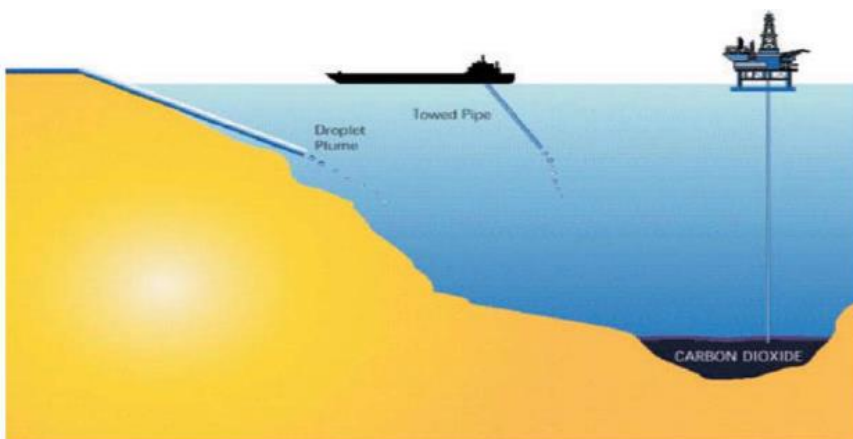


Figure 37: Storage at Ocean depths [59,73]

## 5. Other suggested options

### Basalts

Basalts are volcanic rocks composed of silicates [2] and can be found in great abundance around the world [5,59], as is the most widespread rock on the planet covering large areas of continents and ocean seas [67]. They have low porosity and permeability and low connectivity between the pores, even though they have large volumes. So, CO<sub>2</sub> can migrate almost only through fractures, unless there is an appropriate caprock [5,59].

Nonetheless, basalts can trap CO<sub>2</sub> through mineral trapping, by reacting with basalt's silicate minerals and form carbonates [5,59], which are impermeable formations. So, they

are ideal cap rocks and can prevent the leakage of CO<sub>2</sub> [2]. This is called in situ carbonation process [67].

Its potential for CO<sub>2</sub> storage is therefore very high, even though there is limited knowledge about the stratigraphic structure and the effective reactivity CO<sub>2</sub> with the surrounding formations, needs further assessment [5,48,67,103].

### **Oil or Gas rich shales** [5,58]

Shales rich in Oil or Gas, can be found all over the world, and their trapping mechanism of CO<sub>2</sub> is absorption in organic material. CO<sub>2</sub> injected in these shales can enhance production and reduce CO<sub>2</sub> storage costs. Due to limited research storage potential is basically unknown, however the volume of shales is enormous and provides high expectations. When it comes to site selection, depth and permeability are important for these kinds of formations, as their low permeability is likely not allow injecting CO<sub>2</sub> in large amounts.

### **Cavities/ Caverns**

Underground salt caverns can be manufactured for CO<sub>2</sub> storage [21]. with the aim of storing carbon dioxide for millions of years [58]. A salt cavern's volume could more than 500,000 m<sup>3</sup>.

According to IPCC, 2005 [58], as salt cavern is filled with scCO<sub>2</sub>, volume is reducing, until the pressure within the cavern is equal with the external stress of the salt bed. Although, the capacity of an individual cavern with a diameter of 100 m, might be relative small, only 0.5 Mt of high-density CO<sub>2</sub>, the manufacture of multiple caverns can provide large-scale storage, resulting to high capacity, efficiency and injection flow rate. In order to have efficient storage in this storage site, sealing is essential for leakage and collapsing of the cavern roofs prevention. Furthermore, the disposal of brine solution into the environment might have various impacts.

Solid CO<sub>2</sub> (dry ice) can also be stored in underground facilities, but it demands thermal isolation to minimize heat transfer and loss of CO<sub>2</sub> gas. This could provide a very long-term solution to CO<sub>2</sub> storage in geological formations [21].

### **Abandoned Mines** [5,58]

The suitability of mines for CO<sub>2</sub> storage depends on the physical characteristics and sealing capacity of the mined rock. Extensively fractured rocks, such as igneous or metamorphic rocks are certainly unsuitable for such a project. In contrast, sedimentary rocks, like potassium carbonates, salt or stratigraphic concentrations of Pb and Zn, offer some potential for CO<sub>2</sub> storage. As mentioned above, in case of abandoned coal mines, there is a potential for CO<sub>2</sub> storage, added to coal recovery. However, there is high probability that the overlying carbonate rocks are strongly fractured, which increases the risk for potential leakage.

### **Chemical storage** [21]

Another option is the chemical reaction of CO<sub>2</sub> with natural minerals, such as magnesium silicate to produce carbonate compounds that can be stored permanently. However, the mass of the extracted material would be much more than the mass of CO<sub>2</sub> resulting into higher costs, than the options above. In order this process to be more viable, CO<sub>2</sub> injection should be made in geological formations that already contain those minerals, so that the chemical reaction would take place in situ.

### **2.3.3 Criteria for CO<sub>2</sub> storage:** [5,21]

can be 1) geological, 2) hydrodynamic, 3) geothermal, 4) hydrocarbon potential and maturity of the basins. But, also 5) economic, 6) political and social. However, we will focus only on criteria 1-4.

#### **1. Geological** [21]

Active orogenic belts and continental platforms are not appropriate for CO<sub>2</sub> storage due to not having the necessary rock characteristics, lack of impermeable formations and having faults and discontinuities. On the contrary, sedimentary basins are the suitable sites for CO<sub>2</sub> storage, because they have the necessary porosity and permeability. Moreover, they are identified in areas where energy resources are found and most energy production based on mineral resources takes place.

### **The suitability of sedimentary basins** [5]

As Amvrazi, 2017 [5] mentions, the suitability of sedimentary basins also relies on their location across the tectonic plates.

- Basins created in mid-continent locations or near the boundaries of stable continental plates, are ideal targets for long-term CO<sub>2</sub> storage because of their stability and structure (Atlantic, Arctic and Indian Ocean).
- The possibility of storing CO<sub>2</sub> in basins behind mountains, that were formed by the collision of tectonic plates seems to have quite good prospects (Rock Mountain, Himalayas, Alps, Andes etc).
- Basins located in tectonically active areas (Pacific Ocean, Mediterranean) are not suitable for CO<sub>2</sub> storage due to high potential of leakages.
- Basins located at the edges of tectonic plates, where there is subduction or active mountain ranges are even less suitable for CO<sub>2</sub> storage due to their intense folding and faulting. Basins in convergent boundaries, seem to present volcanic activity, faults and induced seismicity, that can jeopardize the CO<sub>2</sub> storage, by the presence of leakages through the created pathways [21].

The geologic storage of CO<sub>2</sub> in the first two types of basins is less risky than in the convergent basins because of the tectonic stability and general lack of major hazardous geological events [21].

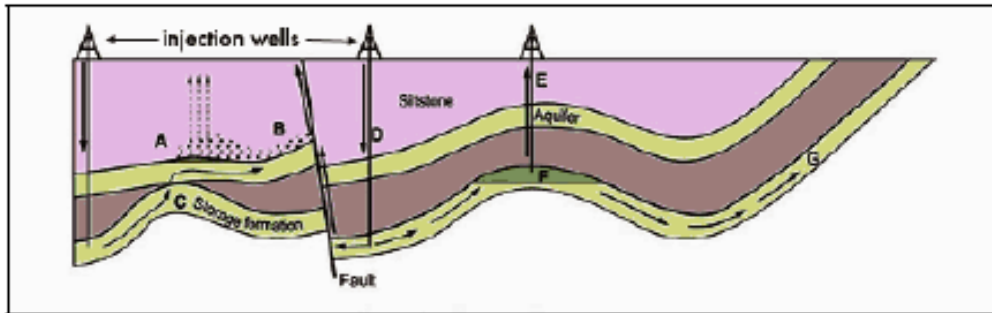


Figure 38: Potential leakage pathways [21]

### Basins that are unsuitable for CO<sub>2</sub> storage: [5]

- have very small thickness  $\leq 1000\text{m}$
- have very poor reservoir and caprock properties
- have intense faulting and fractures
- are in folding zones
- present discontinuities in the sequence of sediments
- have been subjected to significant diagenesis
- their reservoirs are over pressurized

## 2. Geothermal [21]

According to Dimadis, 2009 [21], the geothermal regime in sedimentary basins depends on:

- ✓ The type, age and tectonism of the basins
- ✓ The proximity to heat sources in the Earth's crust, such as magma chambers and volcanoes.
- ✓ Underground heat flow
- ✓ Thermal conductivity and heat generation, which depends on the lithology and porosity of the sedimentary rocks
- ✓ The temperature at the top of the sedimentary sequence

For continental basin in tropic and temperate regions, the temperature ranges from 25-27°C and 4-7°C, respectively. For oceanic basins the temperature at the top of the sedimentary sequence is about 3-4°C. In tropic and sub-tropic basins of with low altitude, CO<sub>2</sub> can be injected either a gas, or in a supercritical state, because the isotherm of 31,1°C is achieved at lower depths (150-500m).

In temperate and oceanic basins CO<sub>2</sub> can be injected either a gas, or in a supercritical state, based on the geothermal regime, pressure and depth of isotherm of 31,1°C. For sedimentary basins located in the Arctic regions, the temperature is about -2°C.

At depths greater than a few hundred meters, like in the shallow oceanic sediments or beneath the permafrost layer in the Arctic basins, the conditions for hydrate compounds are favorable, resulting into a safe separation of CO<sub>2</sub> as a solid hydrate. Thus, the geothermal regime in the basin determine the type and depth of CO<sub>2</sub> injection and storage.

Ajayi et al., 2019 [3], mentions that sedimentary basins are classified as 'cold' due to their low geothermal gradient are more favourable for carbon dioxide storage [7] because CO<sub>2</sub> has higher density at shallower depths (700-1000 m), whereas in the designated 'warm' basins CO<sub>2</sub> gains the required density at greater depths (1000-1500 m). Thus, it is



understood that the depth of the storage formation may also influence the choice of storage location.

### 3. Hydrodynamic [21]

According to Dimadis, 2009 [21], the hydrodynamic regime of water is very important for the injection and storage of CO<sub>2</sub>. Most of the times, H/Cs are get in contact with the underground aquifers. The injection of CO<sub>2</sub> in the active or abandoned deposits, could affect the water flow, and in the case of coal beds, the pressure, the flow and the salinity of the water.

There is a close connection of the sedimentary basin type with the water flow. In basins located at the shelves, the flow is driven by pressure, vertically from shales (aquitards), and laterally outward to the margin of the basins towards the intermediate aquifers. Aquifers are usually under pressure, which can lead technological and safety problems, during CO<sub>2</sub> injection. In basins next to active orogenic belts, water moves laterally outwards and towards its margin, due to tectonic pressure. These waters are usually under pressure, hot and very saline, leading to conclusion that these aquifers are not a suitable storage site. In continental basins, that have suffered uplift and erosion, flow is driven by impact of erosion, vertically to thicker sediments and laterally to aquifers with small thickness.

Impermeable formations and their underlying aquifers are under pressure. These aquifers are suitable for long-term trap and storage of CO<sub>2</sub> toxic wastes - hydrodynamic trapping. In continental basins, flow systems are defined by the topography from the recharge areas (high) to the discharge areas (low) and the pressures of the aquifer formations are usually close to hydrostatic ones, depending on the permeability distribution. In this case, CO<sub>2</sub> must injected into the recharge areas to increase the flow length and trapping time (hydrodynamic trapping).

It is important to be noted, that the depth of 800 m, cannot be taken for granted, as limit for change of gas phase to liquid phase of CO<sub>2</sub>, because it appears that the depth with corresponding pressure at 7.38MPa varies from basin to basin. In order to ensure CO<sub>2</sub> storage, aquifers must be covered by an extensive impermeable or aquiclude rock, to prevent any leakages. Though, there are a few constrains, such as flow pressure and thermal characteristics, flow impacts (gravity and density and viscosity between injected CO<sub>2</sub> and the aquifer) and rock characteristics (porosity, permeability and pressure), which can be overcome with the careful selection of location, injection method and monitoring CO<sub>2</sub> movement.

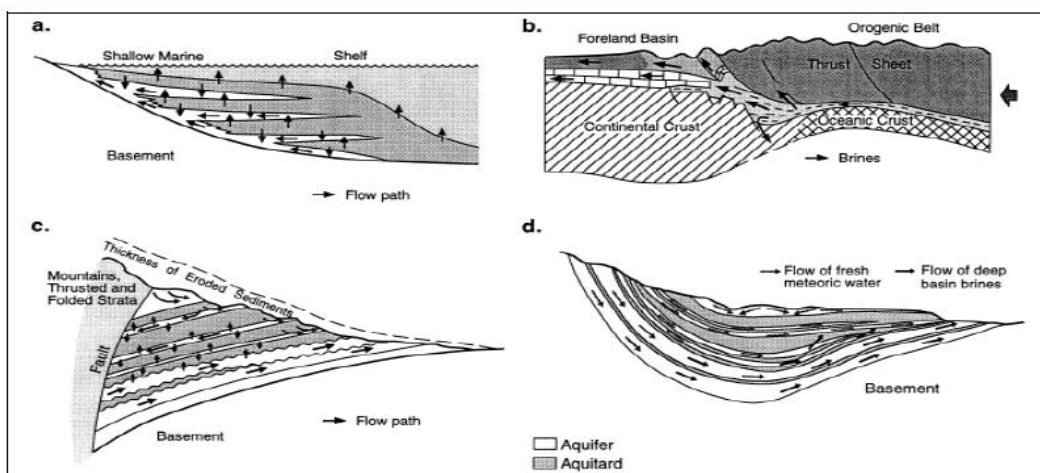


Figure 39:  
Diagram  
displaying fluid  
flow deriving  
from:  
a)compression,  
b)tectonic  
crushing,  
c)erosional  
compound and  
d)topography  
[21]

#### **4. Hydrocarbon potential and maturity of the basins** [21]

In basins with limited or no known energy resource, the only possibility for CO<sub>2</sub> storage are the deep aquifers, rather than coal beds or oil and gas deposits.

If the basin is immature, in terms of exploitation, its geology and hydrogeology information are limited and there is no existence of used or abandoned oil or gas deposits. On the contrary, if the basin is mature, its geology and hydrogeology are well known and understood. In this case, most of the hydrocarbon fields and/or coal beds have already been discovered and are usually in the production process, and some deposits have already been depleted, are approaching depletion, or have been abandoned as not economically viable [5,21]. Also, the appropriate infrastructure is already existing, but the extensive presence of wells could be act inhibitory, as leakage pathways [5].

#### **The effect of impurities on CO<sub>2</sub> storage** [58,59]

Impurities can affect the storage volume, resulting into decreased storage capacity, as they occupy the desired area. In EOR, impurities affect oil recovery, due to reduced mixing ability between CO<sub>2</sub> and oil. Usually, methane and nitrogen are responsible for such effects, in contrast to sulphur oxides which contribute positively to the recovery process. In deep saline aquifers, the existence of impurities affects storage potential, as it reduces the storage. In this case, the increased release of harmful gases, like sulphur oxides, result in negative impacts in implementation of chemical reactions and in the environment. Finally, in coal seams, the impurities are equally responsible for negative and positive effects. The presence of H<sub>2</sub>S or SO<sub>2</sub> in a gas stream, which is stored in coal seams, reduces the ability for storage.

#### **Geophysics**

One of the main roles in deciding the suitable CO<sub>2</sub> storage site, is played by the geophysical methods and especially reflective seismic. This method focuses on [60]:

- the geometry of sedimentary strata, porous reservoir formation and clay sealing layers
- faulting zones detection in sedimentary formations, which might be potential leakage pathways for CO<sub>2</sub>
- porosity and permeability of sustainable reservoirs

Seismic data can provide data for geological structure and its volume, which contribute in deciding the location of the exploratory and exploitation wells [60].

Seismic and Non-seismic methods are very important for the efficient and successful storage of CO<sub>2</sub>, such as 3D seismic, Reflective seismic, Downhole, Crosshole techniques, Vertical Seismic Profiling (VSP), Gravitational, Electrical and Electromagnetic methods and Well logs. These methods provide a “picture” of the sub-surface, including formation rock types, depositional environment, porosity, permeability, fault zones, potential leakage pathways etc. Most of them are analyzed at 2.5 Monitoring.

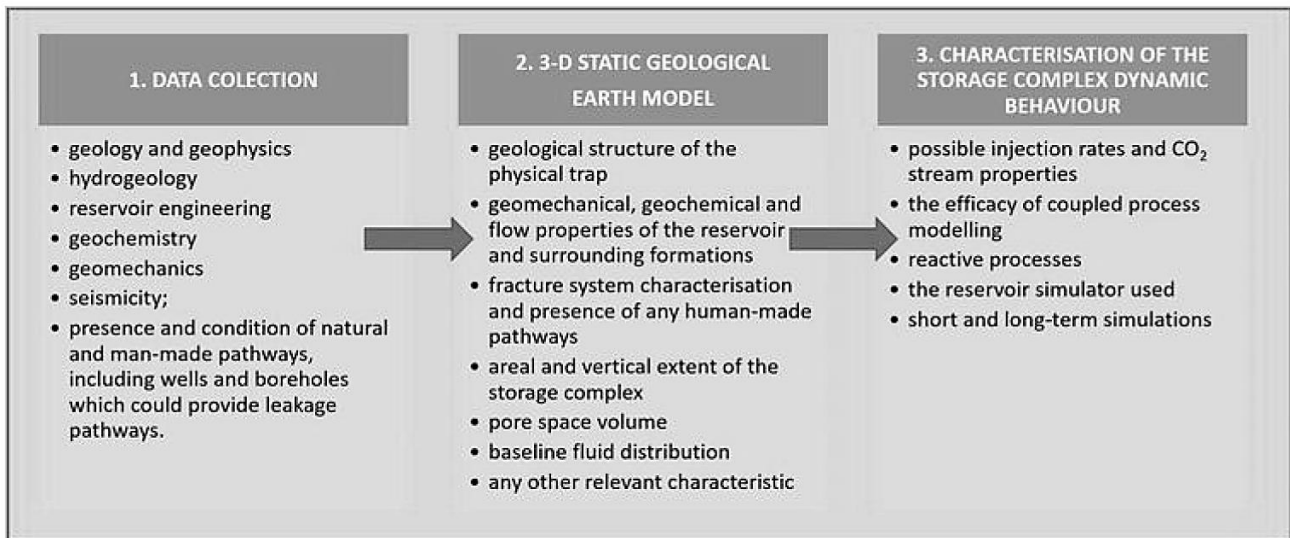


Table 6: The characterization and assessment of the storage complex. [81]

Data collection is the first and most important step in characterizing the storage complex. After collecting the information needed and simulating them, a 3D Static Geological Earth Model is created. This model characterizes the storage complex and includes the cap rock and the hydraulically connected area and fluids. Moving on, the characterization of the storage complex dynamic behavior, is based on CO<sub>2</sub> injection simulations and the 3D model.

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### 2.3.4 Storage Capacity

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**Geology** prevailing in storage sites is mainly affecting their storage capacity. Sedimentary basins are the primary target for large-scale Geologic CO<sub>2</sub> Storage (GCS) and nowadays offshore sites are also being pursued. Capacity characterizes the sustainability and feasibility of a GCS site [82].

The capacity depends mainly on geological characteristics, such as sediment type, porosity, permeability, water saturation, caprock presence, thickness of the formation, percentage of the total area accessible to injected CO<sub>2</sub>, interfacial tension, injection rate, viscosity ratio, fractures and faults etc [4].

Large capacity doesn't necessary mean high feasibility. In some formations there might be large capacity and porosity, but low permeability and insufficient injectivity. In that case more injection wells are required, that probably overcome the projects financial plan. If the capacity area is not in near proximity to large CO<sub>2</sub> sources, the cost is increased since long transportation pipelines are needed. Best-case scenario is when the sink is very close to the source [82]. Nonetheless, according to estimations, there is enough capacity for CO<sub>2</sub> storage for more than a hundred of years [82].

Resource capacity is considered as the total amount of pore space obtainable irrespective the location or the means to access it. [82]. Reverse capacity includes economic, policy, environmental and regulatory restrictions, and limitations, making this type of capacity more measurable and variable due to changes on the above-mentioned aspects [82]. Even though there are variations in capacity, the amount of resource capacity is more than enough, allowing that way the sustainability of the GCS. However, in order the storage site to be viable, considerations must be made about environmental impacts and induced seismicity [82].

According to Bond et. Al, 2017 [11], long term carbon dioxide storage requires the assessment of potential leakage pathways existence and shows the viability of the storage site [11]. Faults and fractures are crucial ways of CO<sub>2</sub> migration to the surface and must be detected to determine the feasibility of the storage site. Faults and fractures can react in a different way when pressurized CO<sub>2</sub> is injected [11]. Faults are responsible for fractures in the formations, that lead to potential leakage pathways. Geological mapping and detailed photometry are used to locate them [11]. The combination of permeability and fracture mapping data is showing that the permeability and the fracture are responsible for the creation of the potential leakage pathways. Sub-seismic fracture networks are also very important [11].

Heterogeneity in fracture properties (connectivity, intensity) is responsible for the creation of higher permeability pathways, which might be sealed over time due to interactions between fluids and rocks. These data play the primary role for the selection of a viable CO<sub>2</sub> storage site. Subsurface exploration, especially for reactivity and flow pathways, but also measurement, verification, and monitoring of the storage site, are responsible for improving the deployment of CCS. The oil and gas industry has put in a lot of effort into understanding the sealing capacity of faults and overburden caprocks, that can store hydrocarbon fluids [11].

**Estimation of CO<sub>2</sub> storage capacity** has many uncertainties due to formation characteristics (heterogeneity) and physics of the processes. The level of uncertainty varies depending on the amount of data available and the method used to estimate storage capacity, which is dependent on the formation type, and can be depleted oil and gas reservoirs, saline aquifers, or coal seams [3].

**Estimation of capacity, depending on the storage site:** [5,59]

- **Oil and gas fields**

Oil and gas fields are excellent sites for geological storage of CO<sub>2</sub>, due to their capacity characteristics. The main storage mechanisms that govern in this case are structure trapping and solubility trapping.

The estimation of the storage space is relatively simpler in these deposits than in the saline-saturated formations and coal deposits, because of the exploration and production of oil or natural gas and the acquisition of numerous data about the area.

Reservoir estimations are based on recoverable reserves, reservoir properties and in situ CO<sub>2</sub> characteristics.

$$GCO_2 = A \cdot h_n \cdot \varphi_e \cdot (1 - S_w) \cdot B \cdot \rho \cdot E \quad (1)$$

$GCO_2$  (mass): estimation of the CO<sub>2</sub> storage capacity of the oil and gas field

$A$  (surface area): Defined area evaluated for CO<sub>2</sub> storage

$h_n$  (length): Net height of the oil and gas column within the reservoir.

$\varphi_e$  (dimensionless): Porosity, by volume defined by net thickness.

$S_w$  (dimensionless quantity): Average water saturation value within the total area ( $A$ ) multiplied by the net thickness ( $h_n$ ).

$B$  (dimensionless quantity): Reservoir volume factor (converts the volume of oil or gas into the corresponding volume occupied under reservoir conditions).

$\rho$  (mass/length<sup>3</sup>): Density of CO<sub>2</sub> at pressure and temperature under storage conditions.

$E$  (dimensionless quantity): Efficiency factor representing the fraction of the total resource volume from which oil and/or gas has been produced but cannot be occupied by CO<sub>2</sub>.

#### ▪ Saline-saturated formations

Saline water formation is characterized as a porous and permeable rock containing water with a TDS (Total Dissolved Solids) greater than 10,000 ppm.

The storage mechanisms that govern in this case are structural trapping, hydrodynamic and residual trapping, dissolution, and mineralization. The latter two types of mechanisms do not contribute at the reservoir estimations.

All sedimentary rocks included in the assessment of saline aquifer resources must have cap rocks composed of shale, anhydrite and evaporites. The thickness of these cap rocks is ignored in the assessment.

$$GCO_2 = A_t \cdot h_g \cdot \varphi_{tot} \cdot \rho \cdot E \quad (2)$$

$GCO_2$  (mass): estimation of the CO<sub>2</sub> storage capacity of the saline aquifer

$A_t$  (surface area): Geographical zone defining the basin or area being evaluated for storage capacity estimations

$h_g$  (length): Gross thickness of the formation for which the storage capacity is being assessed within the basin or area defined by  $A_t$

$\varphi_{tot}$  (dimensionless): Porosity, by volume defined by net thickness.

$\rho$  (mass/length<sup>3</sup>): Density of CO<sub>2</sub> at averaged pressure and temperature under storage conditions in the formation according to  $h_g$  and  $A_t$ .

$E$  (dimensionless quantity): CO<sub>2</sub> storage efficiency factor representing the fraction of the total pore volume occupied by CO<sub>2</sub>. It is based on several formation parameters, including the percentage of the area containing the suitable formation for storage ( $A_n/A_t$ ), the percentage of the storage area with suitable porosity, permeability (hn/hg) and active



porosity percentage ( $\phi_e/\phi_{tot}$ ). It has been assessed that the factor ranges from 0.51-5.4%, for dolomites from 0.64-5.5% and for limestones from 0.40-4.1%.

Geological information, like lithology and geophysical properties of the strata, about the site can be retrieved from existing boreholes or geological exploration or a new appraisal must be done.

## Coal seams

The injected CO<sub>2</sub> in coal displaces the methane through biogenic bacterial activity (in lower ranked coals, i.e. low carbon content) or thermogenic carbonation (in higher ranked coals such as lignite). This process offers also Enhanced Coal Bed Methane Recovery (ECBM), with the recovered methane possibly used as fossil fuel for energy production.

$$GCO_2 = A \cdot h_g \cdot C_s \cdot \rho_{s,max} \cdot E \quad (3)$$

$GCO_2$  (mass): estimation of the CO<sub>2</sub> storage capacity for one or more layers of coal.

$A_t$  (surface area): Geographical area of the coal basin where the storage capacity is estimated.

$h_g$  (length): Thickness of the coal layers, for which the storage capacity is estimated, within the geographical area (A) of the basin.

$C_s$  (percentage): Fraction of adsorbed CO<sub>2</sub> per unit of carbon under reservoir conditions

$P_{s,max}$  (mass/length<sup>2</sup>): Average density of adsorbed CO<sub>2</sub>

$E$  (dimensionless quantity): CO<sub>2</sub> storage efficiency factor representing the fraction of the total volume of carbon that comes into contact with CO<sub>2</sub>.

There is a n important difference between the CO<sub>2</sub> accessibility (absorption and release of methane) of wet and dry coals, mainly due to chemical heterogeneity. So lower rank coals must be tested simulating reservoir conditions (mainly humidity and pressure).

The storage efficiency factor depends on:

- the percentage of the area being that is occupied by the coal beds
- the percentage of these with adsorption capacity
- the area around the injection well that is in direct contact with the CO<sub>2</sub>

For unexploited coal fields this factor ranges between 21-48%.

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## 2.4 Trapping Mechanisms

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**Geology and Geochemistry** are essential in trapping mechanisms. These mechanisms contain a series of geological, physical and geochemical processes [5,59], which their combination is responsible for the effectiveness of CO<sub>2</sub> storage [5].

After the injection and deposition of CO<sub>2</sub> in the storage area, the existence of certain trapping mechanisms is mandatory, to ensure its permanent storage [59]. The most suitable storage sites are the ones that can retain the CO<sub>2</sub> for many years [5,59].

Parameters for long-term storage:

- CO<sub>2</sub> is permanently trapped under a low permeability and dense cap-rock [59], which has large thickness [5]
- CO<sub>2</sub> can be used as a fossil fuel
- CO<sub>2</sub> is converted into solid minerals
- CO<sub>2</sub> is absorbed on the surfaces of the micropores of the coals
- Combination of physical and chemical trapping mechanisms

### Geology in Trapping

#### **Physical trapping: stratigraphic and structural**

Physical trapping is the main trapping mechanism [59]. In geological formations the main criteria of CO<sub>2</sub> storage [59] is the natural trapping of CO<sub>2</sub> under low permeability cap-rocks [5], such as shale or a salt which will prevent the movement of the liquid [59]. Sedimentary basins consist of such closed, naturally defined structures (traps), which are occupied mainly by saline water, oil, and gas [5].

Structural traps occur when we have changes in subsurface's structures [64] and include traps formed by folded or fractured rocks [5,49,59]. Stratigraphic traps are formed by changes in depositional conditions of the formations [5], including lateral and vertical variations in the thickness, texture, porosity, or lithology of the reservoir rock [64]. Both types of traps are considered suitable for CO<sub>2</sub> storage [5]. We have variations and combinations of traps which can be used for geological storage of CO<sub>2</sub> [133]. These traps can store oil and gas in reservoirs for millions of years, the capacity of whom is depending on volume of pore space and reservoir permeability [133]. After injecting carbon dioxide into such a trap, it could take millions of years to travel upwards and reach the surface, due to the sealing capability of the caprock. So, it is important to choose a reservoir that satisfies the requirements of storage [133].

After injection, CO<sub>2</sub> is stored as supercritical fluid or gas, as a function of depth at the associated pressure and temperature [3]. Once the injection is stopped, buoyant CO<sub>2</sub> is moving upwards [3] and is trapped [82], under a fine-grained impermeable caprock [133], due to density difference [3]. Usually, these traps are found in dome, anticline, or fold shaped structures and in order to prevent the upward or lateral movement, they must have vertical and lateral seals. In depleted oil and gas fields, the movement of the CO<sub>2</sub> can also be halted by abandoned wells sealed with cement [3].

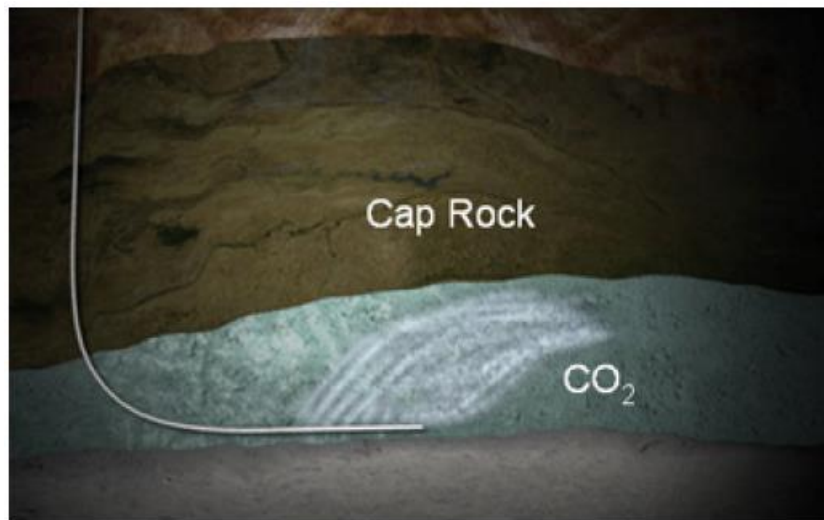


Figure 40: Physical trapping: stratigraphic and structural [15]

### **Physical trapping: Hydrodynamic trapping**

Hydrodynamic trapping takes place in saltwater-saturated formations, in which fluids move very slowly [5,59], over a long period of time [59], and are not surrounded by a closed trapping structure [5]. Hydrodynamic trapping and it is in the future to be the main source of trapping [59]. As CO<sub>2</sub> is injected into the formation, it displaces the saltwater formation and then migrates upward since it is less dense than water [5]. When it reaches the top of the reservoir, it continues to move until it is trapped under a cap-rock, structural or stratigraphic traps [5,49,59] or until it is trapped by capillary pressures in pore spaces (residual trapping) [5]. It is assumed that throughout time a significant amount of CO<sub>2</sub> will dissolve in the formation water and flow with the groundwater [5].

### **Residual trapping**

The injected CO<sub>2</sub> displaces the brine fluids and moves upwards because of density differences (buoyancy) and laterally due to viscous forces [3], as it passes through the porous formation that acts like a sponge [15]. CO<sub>2</sub> continues to flow through the pores and occupy them, but the brine fluid replaces and fills the pores that are already occupied by the carbon dioxide, with water [15,82]. Therefore, some bubbles/droplets of the CO<sub>2</sub> are being trapped in immobile clusters of pores [3,133]. This is called residual or capillary trapping and it is also used in oil storage for millions of years [15]. This type of trapping highly affects the storage of CO<sub>2</sub>. Research have shown that this kind of trapping is able to severely limit

the flow of the injected carbon dioxide and lead to high fractions of CO<sub>2</sub> trapping. Also, they have shown that the injection rate, heterogeneity, and the ratio of viscous to gravity force have the most significant impacts on the final immobilized saturation. Increasing the viscous to gravity force ratio and the heterogeneity will enhance the sweeping efficiency, resulting in more CO<sub>2</sub> trapping as residual gas [133].

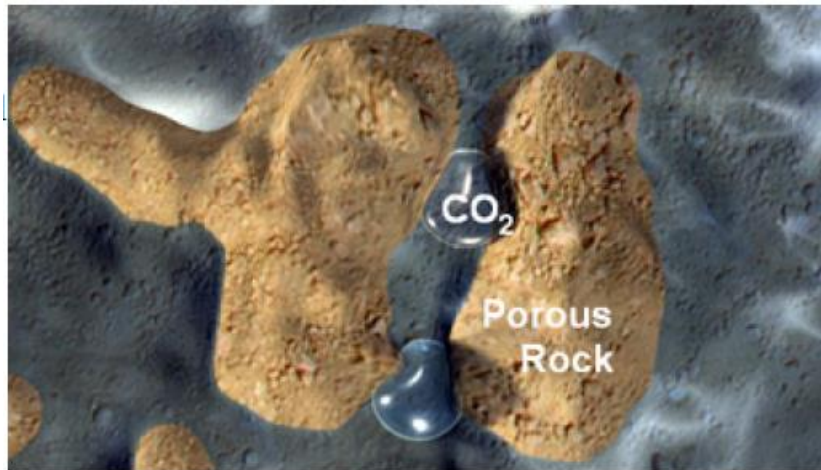


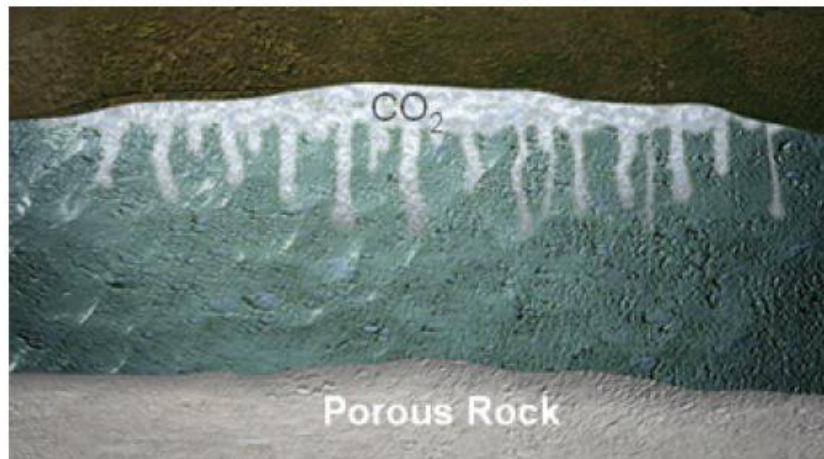
Figure 41: Residual trapping [15]

### **Geochemical trapping [59]**

Geochemical trapping occurs when carbon dioxide's physical and chemical characteristics changes due to series of geochemical reactions with the formation brine and the rock. These reactions will lead either to a mobile or immobile phase. In this way storage capacity is further increased, making this an appropriate feature of long-term storage.

### **Solubility trapping**

Injected as supercritical fluid or gaseous phase carbon dioxide is dissolved into formation fluid, which is saline water or brine [3,82]. Due to buoyancy, it moves upwards reaching the caprock and expands sideways. Since the CO<sub>2</sub> osculates with the formation fluid, CO<sub>2</sub> dissolution and mass transfer are achieved, until our system will equilibrate. As a result, saline water containing CO<sub>2</sub>, becomes denser than the surrounding reservoir fluids [3] and moves downwards in the reservoir, producing diffusion and extra dissolution, which contributes into an increased secure trapping outcome and storage capacity [82].



*Figure 42: Solubility trapping [15]*

### **Mineral trapping**

Through time, the injected  $\text{CO}_2$  will dissolve in water, initiating a variety of geochemical reactions [133] with minerals and other dissolved constituents [82]. This reaction led to the formation of new carbonate minerals [82,133], by trapping the dissolved  $\text{CO}_2$  [133]. This trapping is believed to be relatively slow since it occurs during/after solubility trapping and considered as the most permanent form of storage [3]. However, there is a possibility for these reactions to help in the migration of  $\text{CO}_2$  [133]. These processes depend on the structure, mineralogy and hydrogeology of each formation [133]. In particular, liquid  $\text{CO}_2$  forms a weak acid which reacts with minerals of the surrounding formation. These reactions lead to bicarbonate ions formation with different cations be influenced by the mineralogy of the formation [3].



*Figure 43: Mineral trapping [15]*



Nediljka Gaurina -Medimuree, & Karolina Novak Mavara, 2018 [81], mention that the main concern in large scale CCS is the possibility of leakages, even though well-selected storage sites are capable of retain over 99% of the injected CO<sub>2</sub> for a period of 1000 years. The most important trapping mechanism is the structural/stratigraphic. But the effectiveness of geological storage is based on the physical and geochemical properties of the trapping mechanisms.

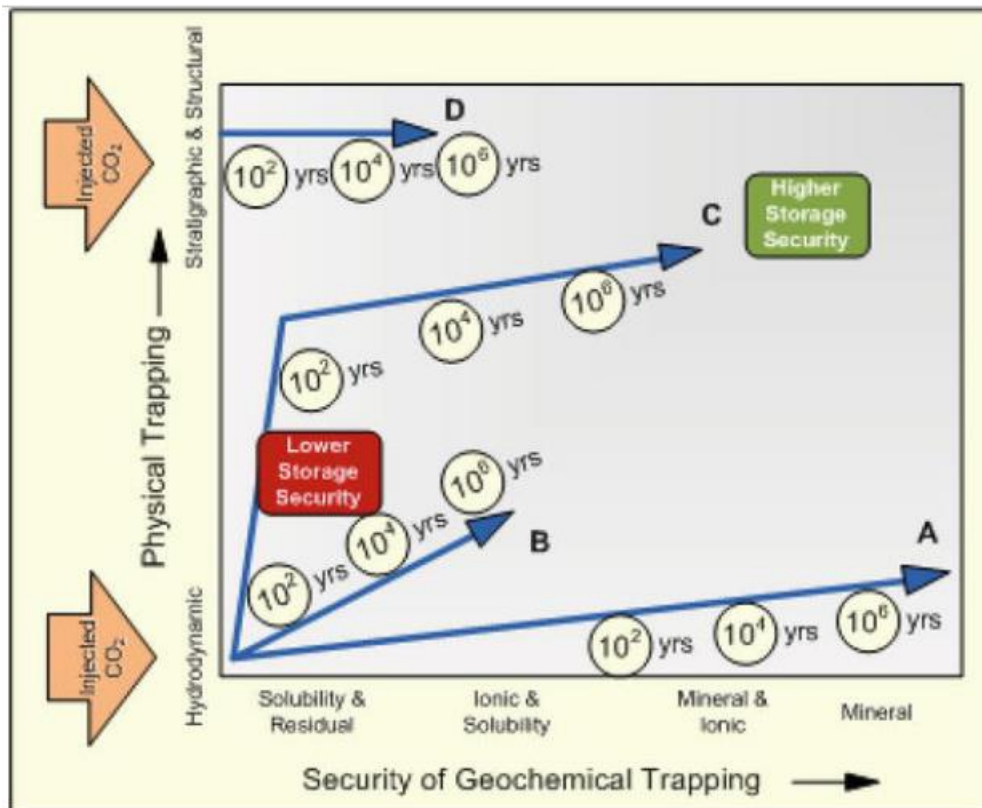


Figure 45: The influence of a combination of physical and geochemical trapping mechanisms on CO<sub>2</sub> security storage (modified after Intergovernmental Panel on Climate Change (IPCC). Special Report on Carbon Dioxide Capture and Storage. Cambridge, UK: Cambridge University Press; 2005. p. 431) Dashed lines are examples of million-year pathways. [81]

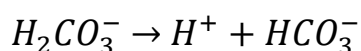
Figure 45 presents four scenarios. Scenario A, B, C represent injection points of CO<sub>2</sub> into hydrodynamic traps, leading to lateral flow of fluids and gas into the formation. On the other hand, scenario D demonstrates injection areas where the flow is physically restricted, such as producing and depleted oil and gas reservoirs. Storage security depends on the distance from the origin and increases with time, as more CO<sub>2</sub> is injected and trapped.



## **Geochemistry in Trapping**

After the captured CO<sub>2</sub> is injected into the subsurface, it initiates various physicochemical phenomena with different evolution times and securing long-term trapping of CO<sub>2</sub>, so that the permanent sequestration of carbon dioxide is feasible [21]. The cement that is placed between the casing and the borehole, is used to prevent fluid migration and to provide well integrity. However, this cement is exposed to various geological fluids making it sensitive [38].

Geochemistry is essential in the impact assessment of CO<sub>2</sub> storage. The corrosive character of CO<sub>2</sub> especially when dissolved, can affect the chemical and physical properties of the wells, the reservoir and their surroundings. Pure CO<sub>2</sub> is considered to be slightly reactive, but when it gets in contact with brine, it forms H<sub>2</sub>CO<sub>3</sub> which is a weak acid that dissociates right away [38].



This reaction decreases the pH of brine and transform it to a corrosive fluid that can affect well materials, rocks and pipelines and jeopardize the success of the CO<sub>2</sub> storage [38].

### **Physical Dissolution/Dilution [21]**

The absorption of CO<sub>2</sub> by physical dissolution relies on the solubility of CO<sub>2</sub> within the solvent rather than a chemical reaction with it. The regeneration of the natural solvent (e.g., methanol, polyethylene glycol dimethyl ether and N-methyl-2-pyrrolidone NMP) is achieved by changing the pressure or temperature. CO<sub>2</sub> is not soluble in water, immediately after the injection is made. The reason behind the upward movement of the injected scCO<sub>2</sub> is its low density compared with water.

### **Dilution/dissolution trapping**

CO<sub>2</sub> is dissolved in the liquid phase (oil or brine) [38]. The dissolution of CO<sub>2</sub> in the water intensifies with the increase of pressure and decreases with the with the increase of temperature and water salinity. The dissolution of CO<sub>2</sub> in water, makes the water denser and therefore it starts to sink deeper, resulting into further mixing between the two phases and increased dissolution of the carbon dioxide [21].

### **Residual trapping**

The plume of injected CO<sub>2</sub> enters the water phase and moves at injection depths that have low flow velocity (<10cm/year). At the end of this plume, the concentration of CO<sub>2</sub> reduces, [21] and it is trapped in the porous spaces, due to capillary effect and surface tension and cannot be mobilized anymore [21,38]. With geological time, this CO<sub>2</sub> can be dissolved in the surrounding water [21].

### Structural trapping [38]

Supercritical CO<sub>2</sub> is trapped in the pores as a buoyant non-miscible fluid depending on the heterogeneity of the storage formation. The percent of scCO<sub>2</sub> which residues in the storage pores is reliant on the rate of dissolution. The dissolved CO<sub>2</sub> makes the brine denser. Due to the difference between the density of the brine and the CO<sub>2</sub>-brine, the mixing time ( $t_{mix}$ ) required for dissolution of the scCO<sub>2</sub> is dependent on the vertical permeability of the porous rock [30].

$$t_{mix} \approx \frac{\alpha L \mu}{k_v \Delta \rho g}$$

$\alpha$ : density ratio of gas/brine

$L$ : reservoir thickness

$\mu$ : viscosity

$k_v$ : vertical permeability

$\Delta \rho$ : density difference between brine and CO<sub>2</sub>-brine

$g$ : acceleration of gravity

Typical Parameters	
$\alpha$	10
$L$	10m
$\mu$	$5 \times 10^{-4} \text{ Pa s}$
$k_v$	$10^{-15} - 10^{-14} \text{ m}^2$
$\Delta \rho$	$10 \text{ kg m}^{-3}$
$\varphi$	0.2

Table 7: Typical parameters in structural trapping

The  $t_{mix}$  for storage sites usually ranges from 1,600 to 16,000 years.

### Solubility Trapping

As CO<sub>2</sub> is dissolving in the aqueous phase, weak carbonic acid is formed, which will separate into H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> ions, with time. Now, they can react with other cations within the formation of brines, leading to insoluble insoluble ionic species. As temperature and salinity increases, CO<sub>2</sub> solubility in formation water reduces [3].

### Mineral Trapping

The interaction between diluted CO<sub>2</sub> and surrounding formation, and the presence carbonaceous minerals can lead to accelerated trapping of CO<sub>2</sub> in stable forms. The formation of these minerals is related to the geochemistry of storage formation (e.g., the presence of clay/silicate minerals) [21]. More precisely, CO<sub>2</sub> integrated into minerals due to chemical precipitation. Dissolution and precipitation control the kinetics of this trapping method. Even though the kinetics of carbonate and sulfate reactions are typically rapid, the kinetics of alumino-silicate mineral reactions, which are more involved, are substantially slower, making CO<sub>2</sub> trapping a slow process [38].

## 2.5 Monitoring

**Geophysics and Geochemistry** play a vital role in CO<sub>2</sub> storage, regarding the amount of injected and stored CO<sub>2</sub>, and monitoring of CO<sub>2</sub> migration [20]. Monitoring the movement of the plume and for possible leakages is critical in the post-injection phase of storage [3,90]. Monitoring provides early detection of CO<sub>2</sub> leakages and aims at the protection of the environment and groundwater [3]. Ensuring safe storage of CO<sub>2</sub> necessitates monitoring during and after injection. Also, it requires surface environment data from geochemical techniques (CO<sub>2</sub> concentration in the air, soil and in the soil water) or satellite and aerial photographs for deformations, and underground geological environment data [60]. The monitoring method depends on the available information about the storage site. Depleted oil and gas reservoirs are considered to have seal integrity, which offers easier monitoring of the injected CO<sub>2</sub> [3].

### Geochemistry

Geochemical monitoring is a vital component of CCS technology. Usually, the most effective geochemical monitoring tools are the chemical tracers, as they can detect, and quantify any potential CO<sub>2</sub> leakages [33,98]. As mentioned from Roberts, J. et. al., 2017 [98] "Tracing techniques are well established in the hydrocarbon and geothermal industry to provide information about reservoir connectivity and flow paths, or to estimate formation residual oil or connate water saturation."

Geochemistry contain tracers of fluid-fluid interactions and fluid-rock processes. For example, gas concentration ratio He/ CO<sub>2</sub> is affected from the dissolution of CO<sub>2</sub> into the brine [20].

Purpose	Monitoring interval	Period	Desired tracer properties
Reservoir characterisation	Reservoir	Site assessment	<ul style="list-style-type: none"> <li>• Must be soluble in dense phase CO<sub>2</sub></li> <li>• Must be conservative (unreactive) to inform on the transport and storage properties of the reservoir rock.</li> </ul>
To validate the presence of the injected CO <sub>2</sub> (i.e. CO <sub>2</sub> attribution) or map the extent of the CO <sub>2</sub> plume.	Reservoir. Possibly overburden units in the case of leakage.	Operation. Possibly post closure.	<ul style="list-style-type: none"> <li>• Must be soluble in dense phase CO<sub>2</sub> and/or CO<sub>2</sub> brine mixtures to track formation water displacement from CO<sub>2</sub> injection.</li> </ul>
To evaluate CO <sub>2</sub> migration and trapping mechanism within the storage reservoir.	Reservoir	Operation	<ul style="list-style-type: none"> <li>• Must significantly partition between different CO<sub>2</sub> phases present in the reservoir to provide information on the amount of CO<sub>2</sub> in these phases.</li> </ul>
To verify CO <sub>2</sub> containment within the storage reservoir	Vicinity of pilot site. <i>Onshore</i> : Shallow subsurface or groundwater, soil and atmosphere <i>Offshore</i> : Pore waters of shallow subsurface or seabed sediments, water column or sea surface.	Operation and post closure	<ul style="list-style-type: none"> <li>• Must be conservative.</li> <li>• The flow properties of 'early warning' tracers must enable early arrival compared to migrating CO<sub>2</sub>.</li> <li>• Tracers for quantifying leakage must be distributed throughout the plume, and must partition into the free CO<sub>2</sub> phase.</li> <li>• The total quantity of leaked CO<sub>2</sub> (to Earth surface) can be calculated from the leak rate if the time since seeping began is known.</li> </ul> <p><math>CO_2 \text{ seep rate} = \text{Tracer seep rate} \times \text{seepage area} \times (CO_2 \text{ tracer quantity ratio}).</math></p> <ul style="list-style-type: none"> <li>• The minimum rate of detectable leakage is dependent on the minimum detection limit of the tracer and the dispersion of the tracer once it is leaking at the surface (Myers et al., 2013).</li> </ul>

*Table 8: The four principal purposes of chemical tracers for CCS. The tracer purpose determines the desirable properties of the tracer. Tracers are largely used to provide information about the CO<sub>2</sub> reservoir [98].*

The tracers are helpful during many stages of CCS, therefore some examples are analyzed below. Firstly, during injection, CO<sub>2</sub> dissolution into the brine may generate fractionation of C and O isotopes, resulting in kinetic isotope effects and differential relative permeability between fluid phases, that can be detected from the traces [20]. Secondly, dissolution and precipitation of minerals can generate elemental isotopic shifts, such as between Ca and Mg, and the use trace metal components can detect brine migration. Finally, tracers can also detect upward migration of CO<sub>2</sub> from overlying saline aquifers, due to acidification [20].

Monitoring injection facilities, storage sites, and the surrounding environment are all vital aspects of long-term geological storage of CO<sub>2</sub> [49,81]. Monitoring purposes are [32,59]:

- a comparison between the actual and modelled behavior of the CO<sub>2</sub> and formation water at the storage site
- detection of significant anomalies
- detection of CO<sub>2</sub> migration
- rapid detection of leakage of CO<sub>2</sub>
- ensure proper functioning of public health and good ecosystem conditions, with detection of significant negative impacts on the surrounding environment (e.g., potable water, human populations or fauna and flora)
- an update assessment of the short-term and long-term safety and integrity of the storage site, including an assessment of whether the stored CO<sub>2</sub> will remain fully and permanently sequestered
- control and optimization of the injection process
- building market confidence in CCS technology

### Type of monitoring tools [3]:

- **Atmospheric monitoring tools:** ensure that there is no leakage of CO<sub>2</sub> into the atmosphere above the formations
- **Near-surface monitoring tools:** link the subsurface and the atmosphere because they provide information on leakages in the subsurface while preventing leakages to the atmosphere if detected in time. Near-surface monitoring is less expensive than atmospheric and subsurface monitoring.
- **Subsurface monitoring tools:** are responsible for movement monitoring of the injected CO<sub>2</sub> plume, to identify its lateral extent and boundaries, but also reservoir pressure changes. They provide a long-term stability demonstration of the CO<sub>2</sub> plume.

## **Geophysics**

Geophysical monitoring and verification of CO<sub>2</sub> injection is necessary during CCS. Effective and long-term CO<sub>2</sub> sequestration relies on 3D subsurface flow model that can predict and match the CO<sub>2</sub> injection and monitoring data, with accuracy, over time (e.g., 25–50 years) and its achieved by taking into consideration [111]:

- core measurements of the fluid-flow
- geochemical impacts of CO<sub>2</sub> on rock properties
- computational simulations and imaging algorithms, with the aim of predicting and imaging CO<sub>2</sub> injection effects in the subsurface
- inversion of geophysical data to ensure accurate estimations regarding the amount CO<sub>2</sub> stored

The selection of appropriate monitoring techniques depends on the technical and geological characteristics of the site as well as the objectives of the monitoring [59].

Monitoring techniques categorized based on their level of maturity and use in similar projects [59]:

### **1. Primary or Direct techniques**

Primary or Direct techniques are commercial technologies and involve the estimation of carbon dioxide within the storage site by using specialized equipment, which will also demonstrate whether the fluid remains inert and whether there are any fractures [59].

During CO<sub>2</sub> injection in EOR projects, CO<sub>2</sub> spreads through the reservoir in a heterogeneous way due to variations in rock permeability. So, the distribution of CO<sub>2</sub> is determined by evaluating the arrival of CO<sub>2</sub> in different production wells [5].

A better approach is the use of tracers as long as gas or gas isotopes are not present in the reservoir system. These tracers can be injected into specific wells, and the arrival time at production or monitoring wells will indicate the CO<sub>2</sub> movement pathways in the reservoir. Furthermore, they can show the movement of CO<sub>2</sub> downstream of the well. However, these techniques can potentially create CO<sub>2</sub> leakage pathways with upward movement. Tracers can provide indications of the lateral distribution of CO<sub>2</sub> within a reservoir. But, in formations with high thickness, multiple sampling provides indications of the vertical distribution of CO<sub>2</sub> in the formation. However, in horizontal wells, the absence of casing (open hole completion) complicates the direct measurement of CO<sub>2</sub> injection [5].

## **2. Secondary or Indirect techniques**

Secondary or indirect techniques are less costly than primary and include a variety of seismic and non-seismic geophysical [5,59] and geochemical methods, to assess the distribution of CO<sub>2</sub> in the subsurface [5]. Seismic techniques focus primarily on wave velocity and non-seismic geophysical methods focus mainly on electrical surveys [59].

### **Seismic geophysical methods**

Seismic methods measure the velocity and energy absorption of waves as they penetrate rocks in the subsurface [5]. The propagation of waves in rocks is varied by the nature of the rock and the fluids contained in it [5]. Usually seismic techniques, include time-lapse seismology, vertical seismic profiling, and cross-well tomography (horizontal and vertical) methods [5].

Thomas L. Davis et. al., 2019 [111] mentions that, “Time-lapse seismology consists of repeating active source seismic surveys in time-lapse mode, or continuously recording passive seismic (micro) earthquake and ambient noise data, in order to image and estimate physical property changes in the subsurface over time.” Seismic 3D techniques evaluate the distribution of faults and the subsurface structures [3]. Multi-component 3D surface seismic provides more accurate information when the geology of the formation is non-uniform and combined with time-lapse can offer valuable information regarding the migration of the injected gas [3]. On the other hand, 4D mode with time-lapse data, can detect the movement of the injected plume and gas leakages [3]. Finally, 2D time-lapse seismic monitoring provide information on costs but are not able to detect plume movement in formations that have complex geometries. Their usefulness is increased at observation and together with cross-well seismic tomography [3]. In general, time-lapse seismic method tracks CO<sub>2</sub> movement inside and above storage formation [5]

Vertical seismic profile (VSP) gives information about leakages and CO<sub>2</sub> migration pathways [3,28] and its distribution within the storage formation [5]. Basically, VSP records the first wave arrivals and reflections from the different geological interfaces. It can also be used combined with seismic reflection method. It provides high resolution image of the subsurface.

Cross-well seismic tomography includes the presence of 2 or more wells. In the case of 2 wells, a source is placed in one well and a receiver array to the neighboring well, to measure the transmitted seismic signal. The collected data are used to generate a reflection image or to map the desired property (P velocity, S velocity etc). Cross-well seismic tomography offers high-resolution reservoir characterization due to the small distance between the source and the receiver. In that way, allows the formation in between the wells to be surveyed and avoids seismic signal propagation through near-surface formations [106]. This method detects the distribution of CO<sub>2</sub> within the storage formation and the leakages through faults and fractures [5].



It is important to be noted, that areas with low injection rate exhibit low or no apparent seismic response. In contrast, areas with high injection rates demonstrate significant seismic anomalies [5]. Also, seismic resolution decreases with increasing depth and is dependent on rock properties [5].

Microseismics is also an effective method of monitoring CO<sub>2</sub>, which can detect microseismic activity in the reservoir due to dynamic changes in pore pressure or the creation of small fractures. Even though microseismic activity is extremely small, it can indicate the pressure changes and possibly the movement of gases within the reservoir [5].

### **Non-seismic geophysical methods**

The most important non-seismic techniques are gravitational methods, electrical and electromagnetic methods, but also well logs.

Gravitational methods determine the movement of CO<sub>2</sub> and measure the changes observed in the subsurface due to density variations because of fluid displacement by another with different density. Gravitational methods do not have the same level of resolution as seismic methods [5]. Gravimetric methods retain low sensitivity and demand a substantial amount of CO<sub>2</sub> injected into the formation before data collection [3]. CO<sub>2</sub> can be detectable if a minimum quantity of a few hundred thousand tones is present which is higher than the one required for detection in seismic methods. This may be enough to detect the path of CO<sub>2</sub>, but not enough to detect possible leaks [5].

Electrical and electromagnetic methods determine saturation changes in the subsurface, by using specific parameters such as resistivity and correlations such as the Archie expression [3], conductivity of the subsurface, so they can detect changes in formation fluid content (e.g., displacement of high-conductivity brackish water by low-conductivity CO<sub>2</sub>) [5]. These methods can track movement of CO<sub>2</sub> within and above the reservoir and detect the brine migration in shallow aquifers. Electromagnetic and electric methods Same parameters and expressions are also used in magnetotelluric sounding, electromagnetic resistivity, electrical resistivity tomography (ERT), and electromagnetic induction tomography (EMIT) [3].

Furthermore, indirect methods such as, electromagnetic, and gravimetric methods, provide images of the sub-surface formations in different time, which present the changes in the structure of reservoir rocks influenced by CO<sub>2</sub> storage [60].

Geophysical logs (sonic logs, neutron logs and density logs) can provide useful information on well properties and reservoir fluids. Considering their ability to map saturation, they can provide information regarding casing corrosion [3]. Well logs are mainly used to measure brine salinity, sonic velocity, and CO<sub>2</sub> saturation. They can detect movement of CO<sub>2</sub> (within and above the reservoir), the brine migration in shallow aquifers and calibrate seismic velocities for 3D seismic surveys [5].

In addition, Tiltmeters can be used to determine the degree of subsurface geomechanically deformation, especially cap rock deformations [3]. Surface deformations have been monitored using InSAR technology, by generating maps using two synthetic aperture radars [3].

### 3. Potential

Potential technologies focus on the study and knowledge of monitoring methods and their relationship with permanent storage of coal in the reservoir and integrity of storage site [59,100].

#### **Monitoring of CO<sub>2</sub> storage**

Preoperational, operational and closure monitoring program must be used to enable the implementation of the CO<sub>2</sub> injection project, increase security and decrease the risk of migration of injected gas, with the aim of environment protection [81].

	Preoperational	Operational	Closure
Basic monitoring	<b>Monitoring program</b>		
	Well logs	—	—
	Wellhead pressure	Wellhead pressure	—
	Formation pressure	—	—
	Injection- and production rate testing	Injection- and production rates	—
	Atmospheric-CO <sub>2</sub> monitoring	Wellhead atmospheric-CO <sub>2</sub> monitoring	—
	Seismic survey	Seismic survey	Seismic survey
	—	Microseismicity	—
Enhanced monitoring	<b>Additions to the basic monitoring program</b>		
	—	Well logs	—
	—	—	Wellhead pressure
	CO <sub>2</sub> -flux monitoring	Continuous CO <sub>2</sub> -flux monitoring	CO <sub>2</sub> -flux monitoring
	Gravity survey		
	Electromagnetic survey		
	Pressure and water quality above the storage formation		

*Table 9. Monitoring program for geologic storage of CO<sub>2</sub> (modified after Benson SM. Potential Liabilities and Mitigation Strategies for CCS. Presentation at WRI Workshop [Internet]. 2007) [81]*

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## 2.7 GIS

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Geographical Information Systems (GIS) play an important role in CO<sub>2</sub> capture and storage, since it provides spatio-temporary analysis, techno-economic feasibility and environmental assessment. Also, it offers emission sources screening and analysis, CO<sub>2</sub> transportation and storage possibilities [129]. The geographic location is highly attributing to CO<sub>2</sub> capture and storage, by providing visual display of spatial relationships and performing screening analysis [17,129].

GIS is a useful tool in CCS projects, because it analyzes and stimulates environmental data, linking it to geographical (spatial locations of CO<sub>2</sub> emission sources and storage sites [12,129]) and descriptive information (properties of emission source and type, characteristics of storage site) to create a new multilayer environmental information.

GIS offers on-screen data visualization as well as through the creation of large and small scale pictures and printed maps [126,129]. Furthermore, it provides a flexible, easily updated database and visualization tool that facilitates the spatial analysis required to solve complicated CO<sub>2</sub> source-to-sink problems [17,129].

CO<sub>2</sub> emission dispersion maps in the regional atmosphere, are created with combination of GIS and various numerical models. Moreover, CO<sub>2</sub> standard concentration in the atmosphere can be compared with predicted and modelled dispersion, at a known geographical location.

A GIS is useful and essential tool for spatially distribution map development, that contains the emission point sources and storage sites.

A CCS project involves:

- CO<sub>2</sub> capture from the point source
- CO<sub>2</sub> transportation to the storage site
- CO<sub>2</sub> injection and storage in the reservoir [124,129].

All of them are presented with several layers in the GIS environment.

### **CCS-GIS database development**

Database is the heart of GIS and provides a wide range of information necessary for spatial analysis and efficient interfacing with other systems and tools.

Appropriate data should be obtained in order to create a database providing information on CO<sub>2</sub> sources, potential storage sites, related infrastructure and associated factors.

If database can enable systems such as decision support system (DSS), it would simplify the screening of potential storage formations, detect transportation fairways, match sources with sinks, and conducy risk assessment (e.g., fault locations and distance from population centers) [78,129].

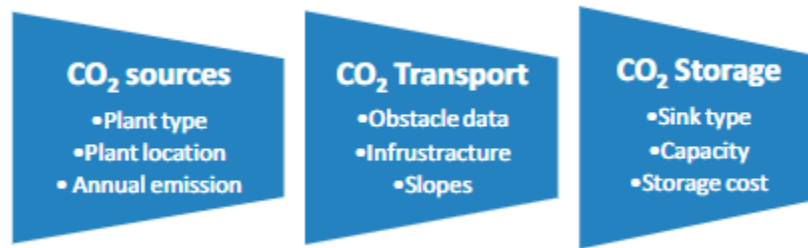


Figure 46: The essential data groups for CCS-GIS database development [129]

### Mapping of CO<sub>2</sub> sources

ArcGIS is a comprehensive collection of GIS software products and a platform for spatial analysis, data management, and mapping [129]. ArcGIS semi-automated mapping and characterization can be used to define the depressions and morphological characteristics, which are used for comparison between mapped depressions due to different lithologies and published data, to interpret possible formation mechanisms [101].

The GIS database for CO<sub>2</sub> source point contains includes:

- plant type and name: power plants, refineries, and industries etc.
- Location: latitude/longitude co-ordinates allow the data to be used in any GIS and provide easier matching source- storage reservoirs [36,129] and source regions provide the transportation options [125,129]
- annual emissions
- emission concentrations [36,129]

### Mapping of storage sites

GIS with "CO<sub>2</sub> sinks GIS inventory" is capable of determining the location and amount of stored CO<sub>2</sub>.

According to Van den Broek et al. [125] necessary data collection includes:

- Location (X and Y coordinates)
- Reservoir Type (aquifers, hydrocarbon reservoirs, unminable coal seams, etc.)
- On- or offshore, affects storage costs
- Start year of injection
- Potential storage capacity
- Depth, thickness, affect storage costs
- Injectivity rate, determines the amount of CO<sub>2</sub> in Mt that can be injected in a well per year.

The feasibility of a CCS project is also depending on GIS. GIS can detect the location and characteristics of potential obstacles (populated areas, buildings, agricultural fields, wetlands, protected areas, rivers, railways, highways etc.) for pipeline network development. Also, it can identify elevation changes (slopes, flat plains) which contribute to the development cost.

In addition, remote sensed satellite technology, is a method that can be used to calculate the biomass and Carbon sequestration value, in quicker and less costly way. Forests, soils, oceans, plants and algae act as natural sinks that can absorb the CO<sub>2</sub> from the atmosphere and GIS and remote sensing, are accurate methods of measuring the amount of sequestered CO<sub>2</sub> [19,109].

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## 2.8 Greece

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The European GESTCO project assesses viable methods for large-scale implementation of CO<sub>2</sub> geological storage and has been implemented in selected areas, including Greece [21]. The purpose of this project is the feasibility assessment on specific storage site types:

- terrestrial/coastal saline aquifers with or without lateral sealing
- low enthalpy geothermal reservoirs
- deep coal deposits containing methane and abandoned coal or salt mines
- depleted or near-depleted hydrocarbon geological formations [21,59]

Apart from GESTCO project, a similar project, NASCENT, has been carried out in Greece, with GEOCAPACITY project currently being developed. Greece's potential locations for long-term CO<sub>2</sub> storage are presented below.

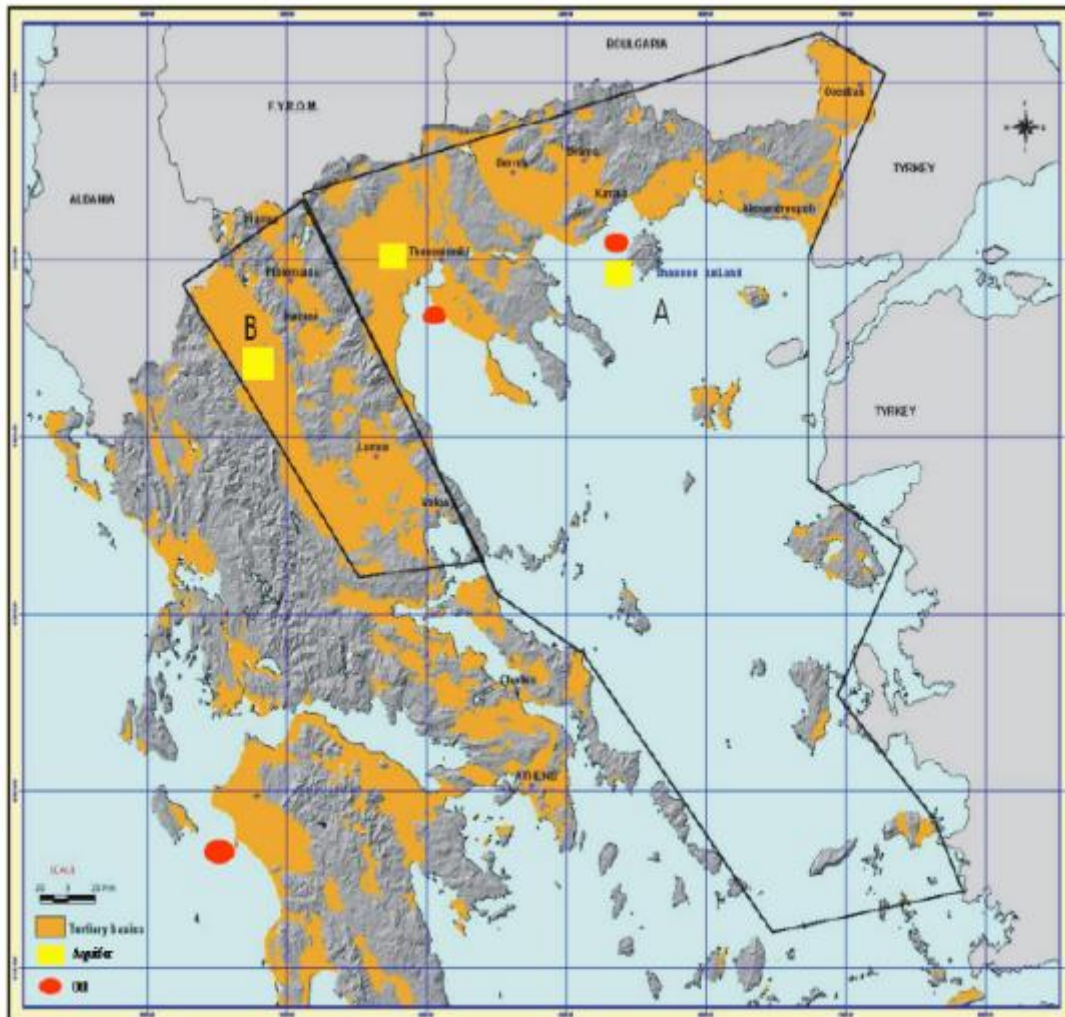


Figure 47: Explored locations during GESTCO project [21]



CO<sub>2</sub> storage capacity in deep water saline aquifers, according to the GESTCO Project:

Deep water saline aquifers	Location	Storage Capacity (Mtn)
Prinos	Coastal	1343
W.Thessaloniki	Continental	459
W.Thessaloniki sandstones	Continental	145
Alexadreia	Continental	34
Mesohellenic Trough	Continental	360
<b>Sum</b>		<b>2345</b>

Table 10: CO<sub>2</sub> storage capacity in deep water saline aquifers, according to the GESTCO Project [21,59]

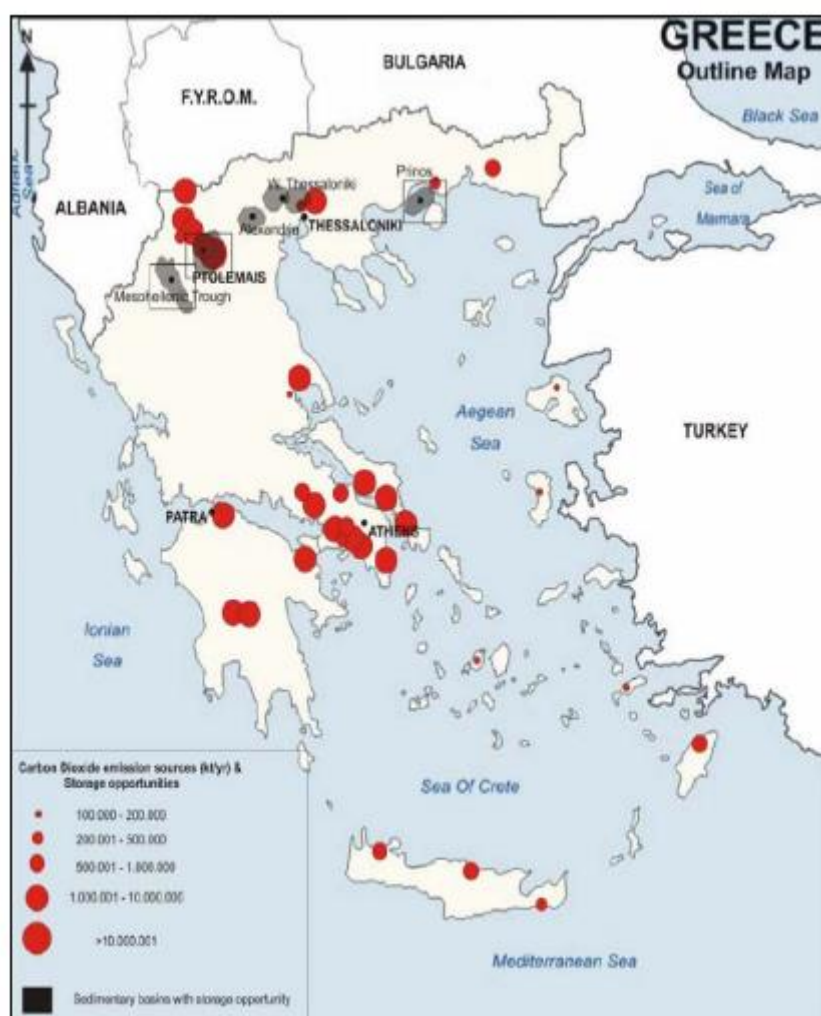


Figure 48: Locations of CO<sub>2</sub> emission source points (power plants and industrial plants) and sedimentary basins with potential for CO<sub>2</sub> storage (source GESTCO Project) [21]

The above locations relate to sedimentary basins with existing hydrocarbon deposits (oil in Prinos and lignite in other cases).

## Characteristics of the sedimentary basins with CO<sub>2</sub> storage potential in Greece

	<b>Prinos Basin</b>	<b>Thessaloniki Basin</b>	<b>Ptolemaida Basin</b>	<b>Mesohellenic Trough</b>
Tectonic stability	stable	stable	stable	intermediate
Area (km <sup>2</sup> )	Small (<1000)	Intermediate (1000-5000)	-	High (5000-25000)
Depth (m)	Intermediate (1500-3500)	Shallow (<1500) & Intermediate (1500-3500)	-	Intermediate (1500-3500)
Deposit-Impermeable formation	Remarkable	Remarkable	Intermediate	Intermediate
Fault activity	Limited	Limited	Intermediate	Extensive
Geothermal (°C/km)	Warm basin (>40): ~80	Cold basin (<30)	-	Intermediate (30-40)
H/C potential	High	Small	-	Small
Maturity	Mature	Not explored	Mature	Not explored
Carbonate Deposit	-	-	Lignite	-
Coastal/ Off-shore	Off-shore	Coastal	Coastal	Coastal
Accessibility	Easy	Intermediate-Easy	Easy	Difficult
Infrastructure	Plenty	None	None	None
CO <sub>2</sub> sources	Few	Few	Important	Important in a 100km radius

Table 11: Characteristics of the sedimentary basins with CO<sub>2</sub> storage potential in Greece [23]

### Sequestration technologies for Greek plants

Research from Center of Research and Technology (CERTH) [37] shows that among the available and applicable technologies, pre-combustion capture, post-combustion capture and oxyfuel combustion, the most suitable appears to be pre-combustion capture. Efficiency seems to reduce with using CO<sub>2</sub> capture technologies, but pre-combustion capture appears to be the lower final investment for the conversion or the establishment of CO<sub>2</sub>-capture power plants. However, these technologies are still at stage of preliminary implementation and their development may overturn these initial conclusions.

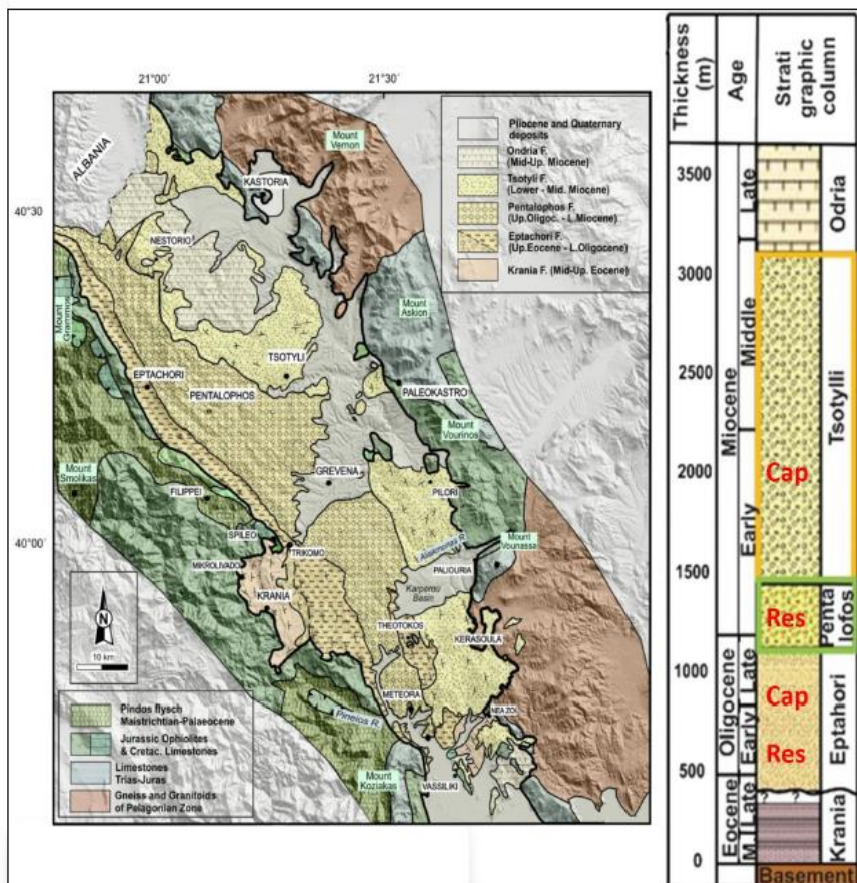
## Mesohellenic Trough

It was developed between the Middle Eocene-Upper Miocene parallel to the Hellenides, with a NW-SE direction [23]. The Mesohellenic Trough is a basin extending over the NW Greece, with a length of more than 200 km and a width of 30-40 km [16,23]. It is characterized as the largest and most important basin of the last orogenic stage - 'molasse-type' basin Hellenides basin [23,122,123]. The basin area ranges from 5,000-25,000 km<sup>2</sup> [16,23]. The thickness of the layers is from 1.5 to 3.5 km and the tectonic stability, offer a favorable storage site [16,23].

The Mesohellenic Trough contains basalts, conglomerates and sandstones which are estimated to provide the necessary space and sealing for the storage of significant amounts of CO<sub>2</sub> [21]. The sedimentary phases include deltaic conglomerates, alluvial rocks, sandstones and submarine clays (turbidites) as well as sandy shelf sediments [23,122]. A significant number of turbiditic sandstones have ~15% porosity, which can reach 25% [21]. Intermediate layers of clay shales provide impermeability. An important advantage is that the basin is located in immediate vicinity with the Kozani-Ptolemaida lignite plants [21]. The selection of Mesohellenic Trough is also due to the proximity to CO<sub>2</sub> emission sources and the possible existence of hydrocarbons [16,23].

To sum up, Mesohellenic Trough is characterized by its:

- significant lateral development (300 x 30 km)
- sedimentary formations with high thickness (up to about 4.5 km in vertical sections)
- changes in sedimentary phases
- thicknesses of the deposits, along and across the basin axis [23,122]



All these reasons above are making her a suitable geological environment for CO<sub>2</sub> storage [16,23].

Figure 49: Geological map of the Mesohellenic Trough and stratigraphic column of the area with indications of the potential CO<sub>2</sub> storage reservoir and cap rock [23]



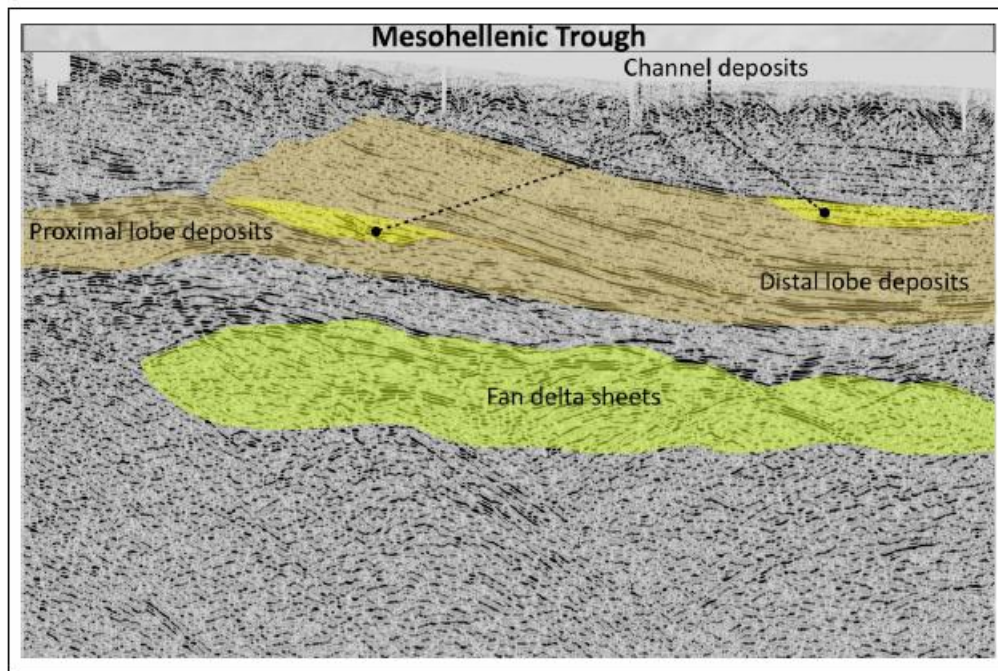


Figure 50: Seismic section with interpretation of sedimentary formations confirming significant thicknesses, that could be potential CO<sub>2</sub> storage reservoirs [23,24]

The main lithostratigraphic sedimentary units that could be used for the development of geological model for CO<sub>2</sub> storage are the following [23]:

- Eptachori Formation, Oligocene age. It consists mainly of cyanic marls (possible Cap rock) and marls with Upper Oligocene pelagic fossils developed on sandy conglomerates (possible CO<sub>2</sub> storage reservoirs) [75,84]
- Pentalophos Formation, Aquitanian age. Includes conglomerates alternating with sandstones [84] which could potentially be a storage site CO<sub>2</sub>. The formation forms a syncline with an axis curvature of NNW-SSE.
- Tsotyli Formation, Lower to Middle Miocene in age. It could potentially be used as a cap rock, because it consists mainly of silty marls with interbedded sandstones, conglomerates, and clastic marly limestones.

From the morphology and lithostratigraphy of the area, it is clear than the western margin contains older formations while the east younger ones [23]. The uplift of the sediments of the western margin during the Middle Miocene and later, resulted in the younger sediments appearing slightly inclined in contrast to the sediments of the western margin. The anticlines and synclines reflect the intense tectonic phenomena as well as the isolated independent formations than can be potential CO<sub>2</sub> storage sites [23].

Tasianas et al., 2016 [118], developed a 3D geological model and estimated that the storage capacity in the Pentalofos reservoir is about 5Gt CO<sub>2</sub> and in Eptachori 722Gt CO<sub>2</sub> [23]. The deepest CO<sub>2</sub> storage point appears to be at the base of Tsarnos at 2544m depth [23]. Tsotyli formation is a suitable cap-rock, which is overlying Pentalofos formation that can potentially store CO<sub>2</sub> [23].

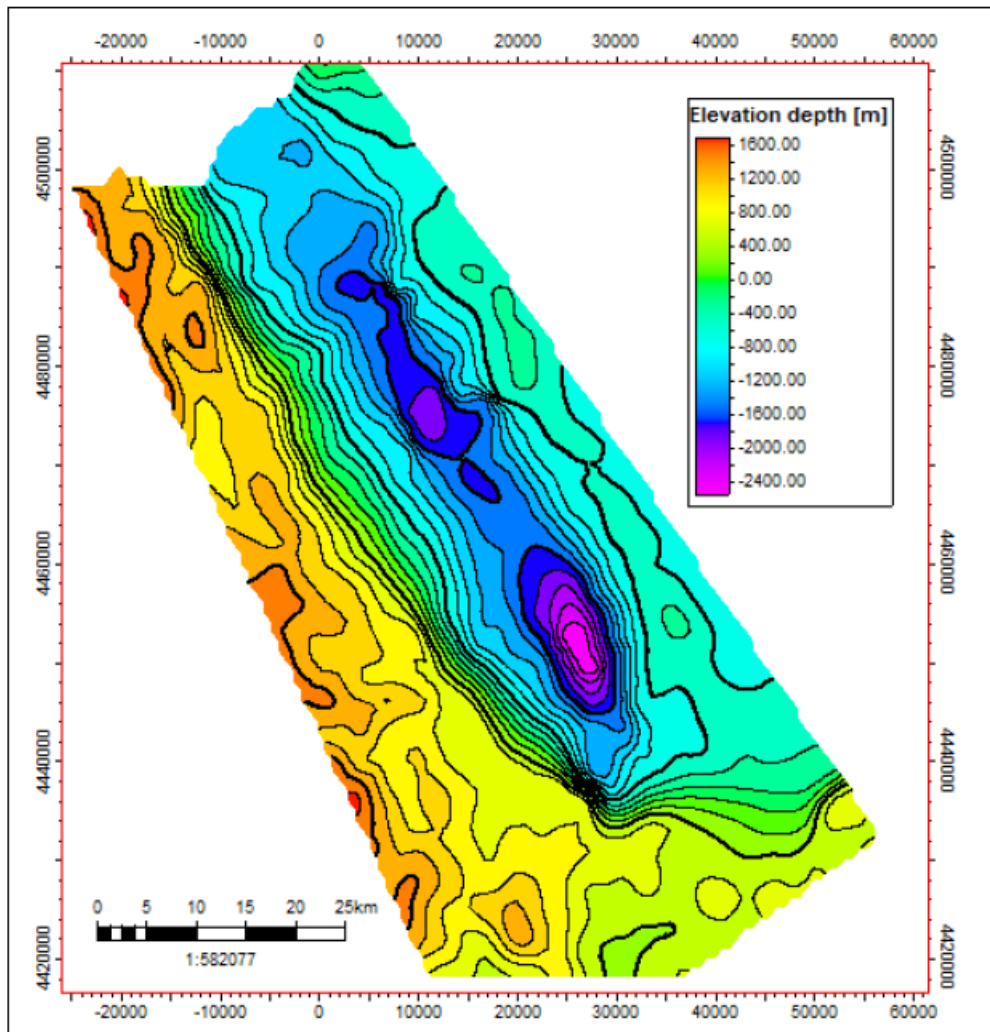


Figure 51: Digitized isopach map of the base of *Tsarnos* (modified after [24,132]) [23]

### **Prinos Basin**

The basin is mainly composed of Upper Miocene submarine ripples, carbonate deposits and underlying metamorphic rocks (gneisses and marbles) of continental origin [23,65]. During Upper Miocene at the formation of Prinos Trench into a lagoon, with the uplift of the South Kavala blocks the connection of the trench with open sea. At the beginning of Pliocene the basin is finally flooded by the sea [23,91].

Prinos basin has been evolved separately from the rest of the N.Aegean and consists of Neogene sediments [21]. The basin is dominated by Upper Miocene evaporite deposits, with a Dolomite-Evaporite zone existing within her [23,91]. It also contains marine turbiditic deposits and alternations of sands and clay [21]. The porosity of the reservoir formations varies between 15 and 20 % [21]. It has a length and width of 38 and 20 km respectively and direction NE-SW covering an area of about 800km<sup>2</sup> and with >6km thickness of the sediments [23,65,70].

Prinos basin has already been explored due to oil drilling operations for several years and therefore the infrastructure exist already [21]. The aquifer is located near and under the pre-

existing oil field, therefore the geological characteristics and data are already known [16,23].

Lithostratigraphic column sediments are subdivided into three units: [23]

- Pre-evaporitic Series (Middle Miocene): mainly clastic sediments (thickness > 1km) that gradually transition to marine [23,91]. These turbiditic sediments, are occupied from hydrocarbons. So, they are suitable oil reservoirs [65].
- Evaporitic Series (Messinian): consists of seven evaporitic layers with alternating clastics with a thickness of 800 m [23,39] usually anhydrite and dolomite [23,93].
- Post-evaporitic series (Pliocene-Pleistocene): consists mainly of marine origin sands, siltstone and clay, with a thickness of 1.8 km [23,86,87,91].

The evaporites act as seals /cap rocks due to their impermeability that can retain hydrocarbons from the underlying reservoirs. Saline domes and evaporite sediments, overlying sandstones and overlying classic unconsolidated sediments, with a total thickness of up to 2.3 km [23,51] can act as a seal/cap rock for the reservoir.

#### **Potential storage sites:**

In the case of Prinos depleted deposits combined with EOR, the oil production will take place simultaneously with CO<sub>2</sub> injection, resulting in an increasing CO<sub>2</sub> zone over the oil zone. This is happening due to continuous oil production that results in larger unoccupied pore volume, that can be filled with CO<sub>2</sub>. So, the storage capacity is increased and with the reservoir thickness range from 1 to 3.5 km, it can be considered as a sufficient site to maintain scCO<sub>2</sub> [23,72].

Moving on to the second potential storage site, the saline aquifer, located 2.4km below sea surface, with a porosity of 18%, presents a potential storage capacity of 1221Mt CO<sub>2</sub> [23,43,71]. The challenge in this case are the pre-existing wells, because even though they will be used CO<sub>2</sub> injection decreasing capital costs, they might not be able to retain CO<sub>2</sub> into the aquifer.

Considering the depleted Prinos deposits, geology (anticline etc.), the existing infrastructures, the existence of evaporites, and no observation of leakages due to seismicity, Prinos Basin is a suitable site for CO<sub>2</sub> storage. On the contrary, in South Kavala deposits, there is observation of leakages, from fault activation [23,93].

South Kavala is an almost depleted natural gas deposit, at 1.7 km depth, that contains 80% methane. The deposit is consists of turbiditic sandstones (1.62-1.73 km) and an impermeable evaporitic cap-rock. The tectonics, lithostratigraphic column and trapping structure (anticline and sedimentary detachment) are almost the same with Prinos deposits. The reservoir is located between the 4<sup>th</sup>, that works as cap rock and 5<sup>th</sup> layer of evaporites [23,92]. Considering all the above, S.Kavala deposit could be a potential CO<sub>2</sub> storage site.



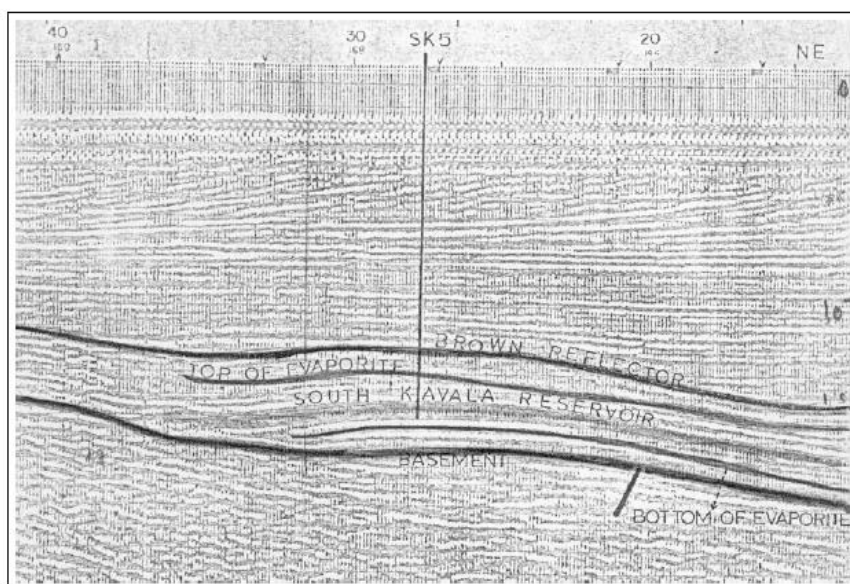


Figure 52: Seismic tomography of aquifer (turbiditic sandstone) and cap-rock (evaporites) of S.Kavala, Well SK-5 [23,92]

## **Florina - Ptolemaida Basin**

### **Florina Basin**

Florina basin belongs to the area of the Western Macedonia Lignitic Centre (Florina-Amyntaio-Ptolemaida-Kozani), where the most part of the country's electricity is produced. It contains large amounts of CO<sub>2</sub> dissolved in the aquifers, that makes her a favorable storage site. After taking into consideration the above, together with the combustion of lignite deposits from the power plants, it reaches the 50% of the CO<sub>2</sub> emissions in Greece. Therefore, any CO<sub>2</sub> emission reduction methods would significantly influence regional and national levels. As a result, Florina Basin represents a suitable location for commercial CO<sub>2</sub> exploitation as an industrial gas and a good natural analogue for risk assessment of CCS technology [16,23].

A research of (Koukouzas et al., 2015) regarding the CO<sub>2</sub> leakage helped into understanding the storage site, in means of lithology and permeability of formations, reservoir and caprock. The leakage appears to be located in sandstones and Neogene conglomerates, at a depth of 300 m (Mesochorion) and the use of a 3D geological model is able to identify the CO<sub>2</sub> leakages at shallow depths and their pathways [23].

CO<sub>2</sub> in Florina Basin has volcanic origin and is mainly found in Miocene fluvial sandstones and limestones [23,61]. The sedimentation environments of Florina Basin are favorable for the CO<sub>2</sub> storage and with the appropriate stratigraphic changes, CO<sub>2</sub> cannot escape [23,61]. The cap-rocks in this region (e.g. Mesochorion area) are mainly composed of clay sediments, but in general there is lack of overlying layers that can trap CO<sub>2</sub> [23]. The faults which were created before and/or during the formation of the basin, act as CO<sub>2</sub> leakage pathways towards the surface [23]. In conclusion, CO<sub>2</sub> may be migrating, through the pores of permeable geological formations, and by dissolving in water [23,69].

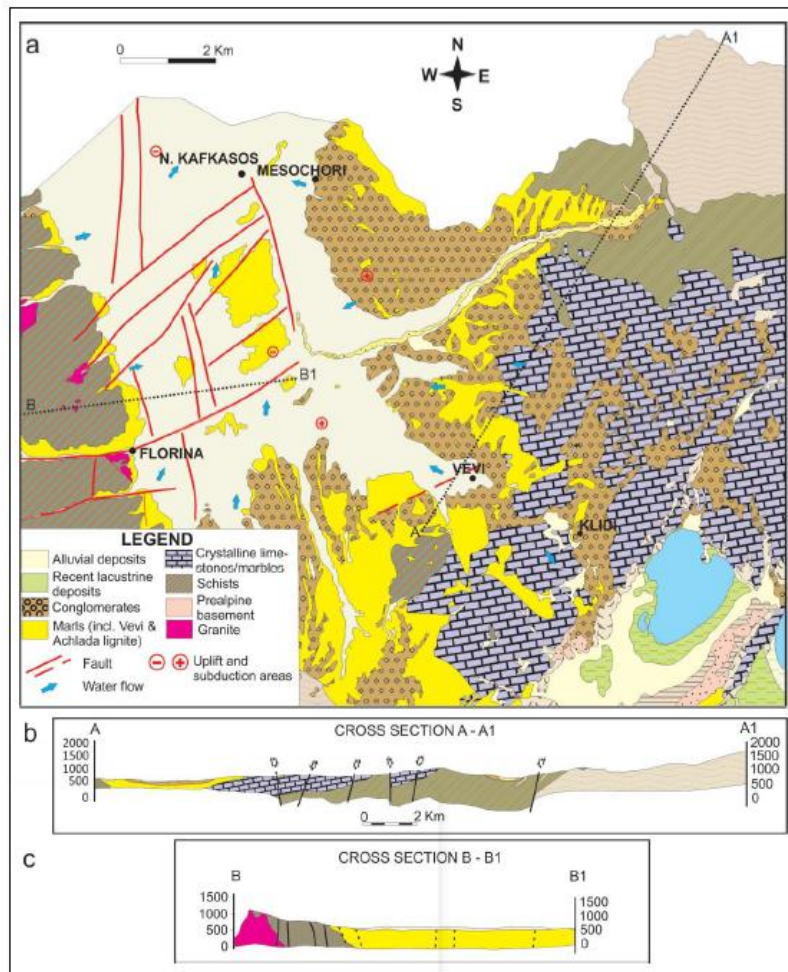


Figure 53: Geological map of the Florina Basin showing the distribution of the lithology and b) and c) are geological sections A-A1 and B-B1 respectively (Koukouzas et al., 2015 [23,69])

## Ptolemaida Basin [21]

Ptolemaida Basin is the most interesting, energetically, macrostructure of Greece due to the exploitation of lignite reserves. It was formed in the Neogene and contains conglomerates, sands, marls and lignite-bearing formations. Even though, this potential CO<sub>2</sub> storage site requires further development to be proven suitable and feasible, its location is favorable because it is close to the power plants.

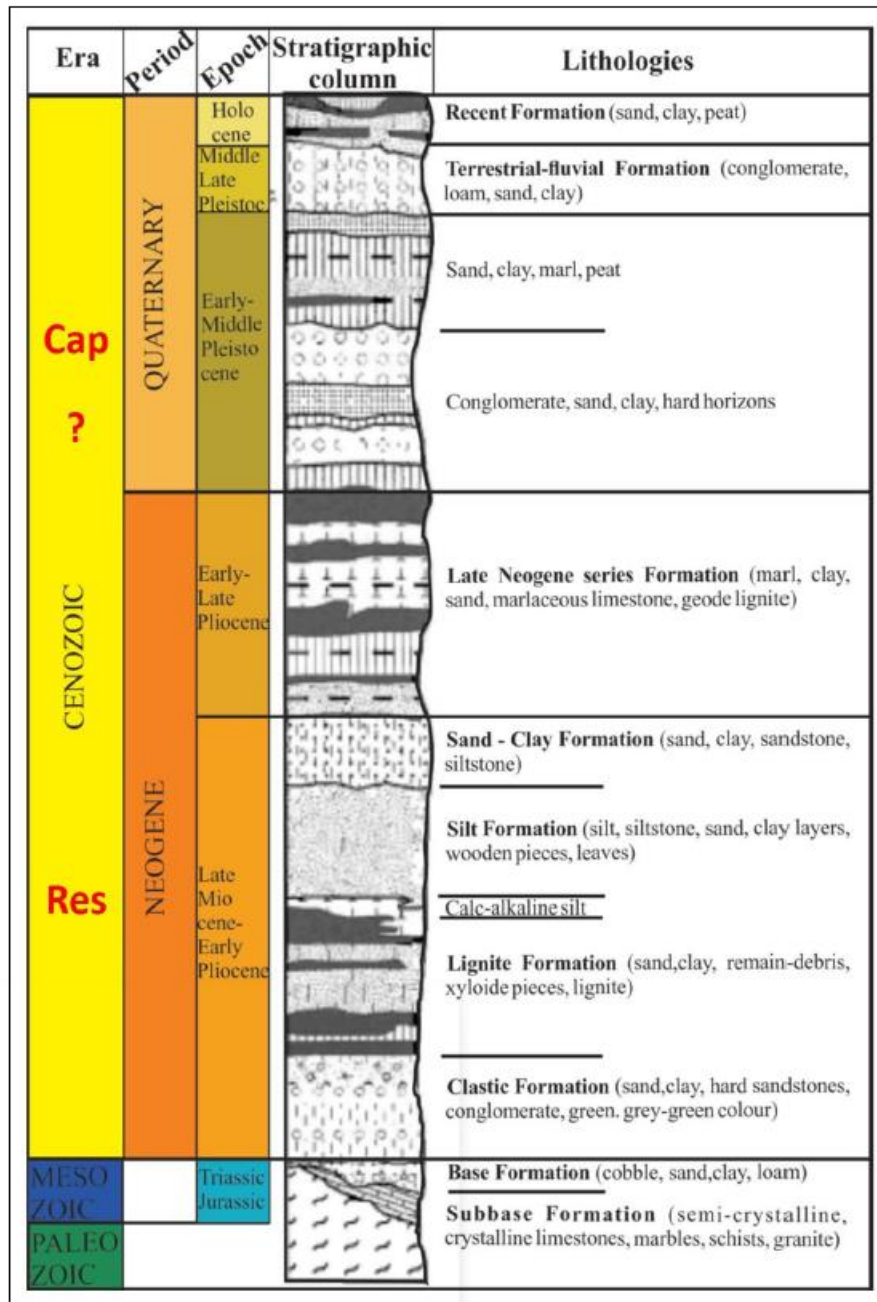


Figure 54: Lithostratigraphic column of the system of the Florina-Amyntaio-Ptolemaida system (Koukouzas et al., 2015) [23,69]

### Western Thessaloniki

In this case the aquifer is located in the basin of Western Thessaloniki, and it is considered as suitable for CO<sub>2</sub> storage site [16,23]. It extends over an area of more than 4200 km<sup>2</sup> onshore and an offshore area of 4000 km<sup>2</sup>. Furthermore, it is assessed as a tectonically stable area with limited presence of faults [16,23]. The basin is mainly composed of conglomerates, sands, clay, but also there are local occurrences of limestones and marls. The base is consist of high grade metamorphic rocks (Axios zone). The overlying sediments mainly composed of Oligocene Flysch a thickness of ~1200m [23]. The brackish

formations aquifers in the sandstone, have a thickness of 500 m, and a sand/clay ratio between 40% and 90%. The depth ranges 900-2400m, which provides the potential for CO<sub>2</sub> storage and maximises it in cold basins [23]. Porosity varies from 5% to 20% and permeability till 120 mD [23]. Therefore the presence of saline aquifers, tectonic traps and a cap-rock composed of clay, are the main reasons that ensure the ability of this basin to store CO<sub>2</sub>.

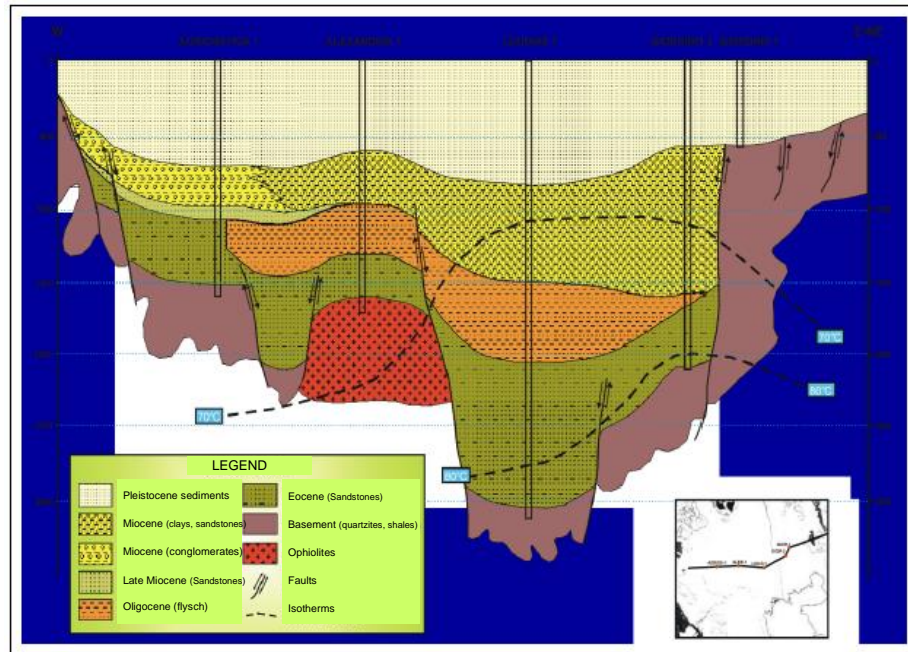


Figure 55: Geological section of Thessaloniki Basin [23,131] Modified

	<b>Western Thessaloniki</b>	<b>Western Thessaloniki (sandstone)</b>	<b>Alexandria</b>
Location	terrestrial	terrestrial	terrestrial
Aquifer depth (m)	1200-2200	2400	900
Area (km <sup>2</sup> )	1700	1700	70
Thickness (m)	100	21	180
Porosity (%)	10	10	8
Pore Volume (km <sup>2</sup> )	10.20	3.21	0.76
Storage Capacity (Mt/CO <sub>2</sub> )	460	145	35
H/C potential	No	No	No
Caprock quality	Very good	Very good	Good
Risk of CO <sub>2</sub> leakage	Small	Small	-

Table 12: Summary table of the characteristics of underground formations [23,53,74]



## Volos

Basaltic rock's physicochemical properties contribute in carbonate mineral precipitation through the interaction of Ca-Mg-Fe rich minerals with carbonic acid, derived from the dissolution of injected CO<sub>2</sub> in water [16,23]. The formed minerals are mainly composed of calcite, magnesite and siderite, which provide the potential for long-term and safe storage of CO<sub>2</sub> [16,23].

The Pleistocene basaltic and trachyte lavas in Microthives and Porphyrio, formed due to the back-arc extension of the Aegean, that is responsible for the high temperature groundwaters. Their geochemical characteristics suggest that they are alkali basalts and are related with Ocean Island Basalts (OIB). The porosity mostly ranges between 15% and 23% [23,68].

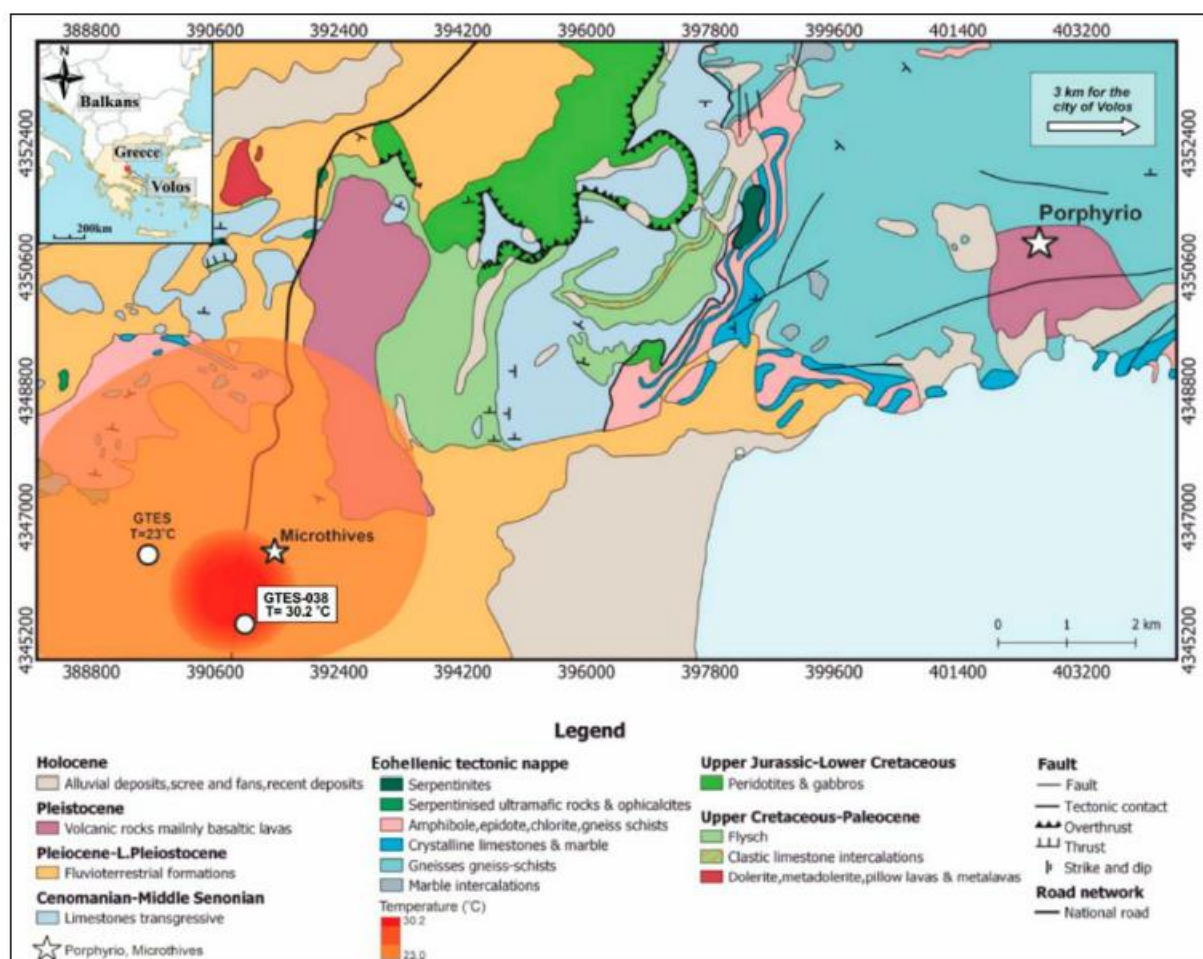


Figure 56: Geological Map showing the groundwater temperature regime in the area of Mikrothives [23,68]

In conclusion, the physical and chemical properties characteristics of Basalts are making them a potential CO<sub>2</sub> storage site. More specifically, due to [23]:

- low alteration degree
- alkaline composition of unsaturated silica
- presence of Ca-bearing minerals
- high porosity
- increased heat

Basaltic rock proximity to the sea, enhances the exploitation opportunities of the unlimited water resources during CO<sub>2</sub> injection [23,69]. This potential reservoirs are located near the industrial area of Volos, making the development of a project, more economically feasible. The primary assessment is referring to 82,800 tonnes of CO<sub>2</sub> storage capacity in Mikrothives and 27,600 tonnes in Porphyrio [23,69].



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## ***Conclusion***

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The role of Geosciences in Geothermal Resources and CCS is significant and observed along of all stages, with Geology having the primary one. Geothermal resources and CCS are eco-friendly technologies, which contribute to the economy. As mentioned above, Greece, due to her complex geological setting and variety of geological formations, has shown a huge potential for both technologies. What remains is social, political and mainly economic barriers, that limit their implementation.

However, studies [37,79] have been conducted regarding the combination of CCS and geothermal technologies. This innovative technology shares the injection wells, with the aim of reducing emissions faster, but also the costs. Instead of water it uses CO<sub>2</sub> as heat transfer fluid, achieving less water consumption and pump costs. So basically, it uses the same aquifer to provide heat, but also for (dissolved in brine) CO<sub>2</sub> storage. Since this technology is at a mature level, it can ensure safe storage. Additionally, this technology holds the key to change public perception regarding these two technologies. Finally, the knowledge, tools and monitoring used in CCS, can be applied to geothermal energy.

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