Storage of anthropogenic CO\(_2\) in geological formations (CCS technology) is one of the options to reduce climate change. The author examines the sedimentary formations in North Hungary, which can have the potential for CO\(_2\) storage. In the studied area, there are Oligocene, Miocene and Pannonian porous sedimentary rocks, which can be storage sites if further examinations prove their suitability.

1. Introduction

In the scientific literature, there is a strong consensus that global surface temperatures have increased in recent decades and that the trend is caused mainly by human-induced emissions of greenhouse gases [1]. No scientific body of national or international standing disagrees with this view. Conventional predictions of future temperature rises depend on estimates of future GHG emissions and the climate sensitivity. Models referenced by the Intergovernmental Panel on Climate Change (IPCC) predict that global temperatures are likely to increase by 1.1 to 6.4 °C between 1990 and 2100 [10]. Others opinions state that temperature increases may be higher than IPCC estimates.

In 1997 in the Kyoto Protocol 37 countries committed themselves to a reduction of CO\(_2\) (and other greenhouse gases) below the 1990 level. By September 2011, 191 states signed and ratified the protocol (USA hasn’t ratified).

One of the options to reduce carbon emission is the application of CCS (Carbon Capture and Storage), in other terms CO\(_2\) sequestration technology. CCS involves capturing CO\(_2\) at coal- or gas-fired power stations and industrial facilities (steel mills, cement plants, refineries etc.), transporting it by pipeline or ship to a storage location, and injecting it via a well into a suitable geological formation for long-term storage. Industrial-scale research projects on CCS have been conducted in Europe, the United States, Canada, Australia and Japan since the 1990’s.

There are four major possibilities for the geological storage of CO\(_2\): (1) injection into saline aquifers, (2) injection into depleted gas fields, (3) injection into oil fields with enhanced oil recovery (EOR), (4) injection into unmineable coal seams, possibly with enhanced coalbed methane recovery (ECBM) [4].

In Hungary all the four options are potentially available. In the frame of the recent study we review the sedimentary formations in the North Hungarian area, which can potentially be taken into account for CO\(_2\) sequestration

2. Storage of carbon-dioxide in saline aquifers

A saline aquifer can refer to a porous and permeable sedimentary rock body saturated with non-potable water, from which the water can be drawn, and into which fluids can be injected to be stored for a longer period of time. The water of saline aquifers has usually
high dissolved material content (a few percent to tens of percent). Saline aquifers are believed to have the greatest potential to store CO$_2$.

The size of a saline aquifer for CO$_2$ storage is $0.05–50$ km$^3$. The porosity of a potential CO$_2$ reservoir is typically 5–30%, with pore diameters of nm-mm. Suitable aquifers should have a caprock of low permeability to minimize CO$_2$ leakage. Injection of CO$_2$ into deep saline reservoirs would use techniques similar to those for oil and gas fields. The world’s CO$_2$ storage capacity in saline aquifers is estimated 400–10 000 Gt, while the annual CO$_2$ emission is 27 Gt [8]. In the light of these numbers this storage option seems to provide unlimited opportunities but as our knowledge about the deep-seated layers is very limited we have to take a lot of uncertainty into account.

The behaviour and transport of any fluids in rocks are influenced by the density, viscosity, solvability and miscibility of the fluid. All these parameters for the CO$_2$ are desired to be high in order to get the optimal storage conditions. This will help prevent it from escaping upwards since a dense fluid tends to descend. The efficiency of CO$_2$ storage in geological media, defined as the amount of CO$_2$ stored per unit volume increases with increasing CO$_2$ density. The high viscosity of the injection fluid makes injection more difficult, but on the other hand it prevents CO$_2$ to escape from the reservoir. Both solvability and miscibility also have to be high because when CO$_2$ is coupled with the in situ fluid already present in a reservoir rapid escape from the reservoir is prevented [9].

In order to get the optimal fluid conditions, CO$_2$ should be in supercritical stage. For this reason, the sequestration can be applied to rock bodies at a depth of about 800 m. Taking the world-wide average geothermal gradient, this depth corresponds the pressure and temperature values for the critical point of CO$_2$ (31.1 °C temperature, 7.3 MPa pressure). At these values the density of CO$_2$ is 50–80% of that of the water. The CO$_2$ is partly dissolved in the formation water, partly fills the open pore spaces and due to the buoyancy effect it is enriched in the upward arching structures. In some formations it would slowly react with cations to form carbonates, which would lock up the CO$_2$ essentially permanently [4].

Based on these conditions a saline aquifer, which is a potential CO$_2$ reservoir, should complete the following requirements:

- large horizontal and vertical extent for the storage capacity,
- high porosity and permeability,
- impermeable caprock above the storing unit,
- the geological structure restrains CO$_2$ from escape,
- tectonically stable (no joints, faults, folds as potential paths for escape),
- isolation from fresh water bodies.

These requirements are usually fulfilled by porous sandstone formations. A potential problem that might occur is that if the pressure increases to a high level it can potentially fracture the seal above the aquifer and push salt water from the aquifer into shallower, possibly fresh water layers. With large-scale injection being considered, this pressure build-up issue needs to be examined closely.

The most significant sequestration project related to saline aquifers is the Sleipner project in Norway. The project started in 1996 and annually 1 million tone of CO$_2$ have been injected into the Utsira Formation at a depth of 800–1000 m. The total injected amount is planned to be 20 million tone. The reservoir rock is sandstone, covered by thick, impermeable shale.
3. Geology and CCS potential of the examined area

The examined area embraces the southern foreland areas of the Cserhát, Mátra and Bükk Mountains and the northern margin of the Hungarian Plane. Basically, the karstified carbonate rocks with large fresh water reserves of the Bükk Mountains and the thick volcanic formations of the Mátra and Cserhát Mountains have to be excluded.

In the followings we describe the rock types of the examined area in a chronological order, with a special emphasis on the CCS potential.

3.1. Mesozoic formations

Although Paleozoic rocks outcrop in the northern part of the Bükk Mountains, it is built up mostly by Mesozoic carbonate rocks and slightly metamorphosed shale (Figure 1). The Triassic carbonate formations are of several kilometers in thickness containing valuable karstwater. The Jurassic clayey shale in the South Bükk have low porosity and permeability, that is why cannot be considered as potential CO₂ reservoirs.

![Figure 1: Geological sketch of the examined area. Black lines marked with numbers show the directions of the geological sections in Figure 2, 3 and 4 (After Haas et al., 2001)](image)
3.2. Paleogene-Neogene basins

The Paleogene-Neogene basins are built up by variable sedimentary rocks, with a thickness of maximum 5 km. In the Carpathian Basin this area represents the largest vertical and horizontal extent of the Eocene–Oligocene–Miocene sequence. The deepest part of the basin is situated below and in the southern forefront of the Cserhát Mountains. From south, the basin is margined by the Bugyi–Tura–Hatvan–Mezőkövesd blocks, from the west by the Pilis Structural Zone and from the east by the Tokaj Mountains [6].

3.3. Tertiary formations

In the western part of the basin the basement of the Tertiary sequence is built up by Veporian crystalline metamorphites. In the eastern part the basement is formed by the Bükk-type Triassic carbonates, shales and a fragment of the Darnó Ophiolite Complex [2].

3.3.1. Eocene formations

The marine transgression in the area started in the Late Eocene and resulted the formation of light grey limestone and limy marl (“Szépvölgy Limestone”, “Buda Marl”). The “Szépvölgy Limestone” contains abundant fossils. The thickness of the Eocene formations is 30–40 m [2]. Because of the low porosity, the low thickness and the limited extend the Eocene formations are generally not suitable for CO$_2$ storage, although in the Mezőkeresztes–Demjén–Fedémes–Bükkszék oil fields the exploitation takes place partly from Triassic and Eocene fractured carbonate rocks [3].

3.3.2. Oligocene formations

During the Oligocene the transgression became more extended in the North-Hungarian area. The marine area was separated from the opened ocean and reductive environment, euxinic facies became characteristic. This sedimentary environment favoured the formation of the dark grey, bituminous “Tard Clay” in the Early Oligocene (Kiscellian Age). This formation is considered as the source rock of the oil fields at Bükkszék. Its thickness varies from 30 to 100 meters.

Following the formation of the “Tard Clay”, there was an uplift and the area became a dry land for a short time. Then, as a result of the new transgression, the “Kiscell Clay” was formed in the open marine areas while in the marginal parts the Hárshegy Sandstone was deposited. The latter one is found outside the examined area, In the Buda Mountains and the Esztergom Basin. The “Kiscell Clay” is similarly bituminous to the “Tard Clay”. It is thought to be the source rock of the hydrocarbon fields of the Hungarian Plain. In the central parts of the basin, its thickness exceeds 1000 meters [2].

In the Late Oligocene regression started in the basin area, which resulted the deposition of shallow marine sediments. In the western part of the basin the “Törökbálint Sandstone” was deposited, which is a slightly consolidated rock with pelitic matrix. Its thickness is about 250 meters.
In the eastern margin of the basin the Eger Formation was formed, which represents a continuous regressive sequence. The lower unit is represented by glauconitic sandstone in a thickness of 3–40 m, it is covered by molluscan clay of 40–50 m, then shallow marine sandstone in similar thickness. In the Nógrád–Cserhát–Ózd–Rimaszombat area the “Szécsény Schlier” was deposited in a thickness about 800 m. In the marginal parts shallow marine glauconitic sandstone (Pétervásár Formation) was formed. At the end of the Oligocene the Paleogene the sedimentary sequence filled up the Paleogene Basin the area was lifted and became a dry land [2], [5], [6].

As for the CCS potential of the Oligocene sequence the followings can be summarized:

− The reservoir rocks of the Mezőkeresztes–Demjén–Fedémes–Bükkszék oil fields are Eocene and Triassic fractured limestone, Oligocene sandstone and Miocene pyroclasts. Because of the low porosity and permeability of these rocks the exploitation is problematic, which is even increased by the high density of oil. The depleted parts of the reservoir can be taken into account as CO₂ storage sites.
− The Lower Oligocene “Tard Clay” and “Kiscell Clay” are not suitable for CCS (Figure 2, 17; Figure 3, 23; Figure 4, 17).
− In the Late Oligocene sedimentary sequence there are certain formations, which have CCS potential as they are deep-seated, porous and permeable. These are the marine Egerian-Eggenburgian sandstones between the Tura-Hatvan Blocks and the Cserhát Mountains (Figure 2, 18). The problem can be that their position is too deep (2000–3000 m), which would significantly increase the injection costs.
In the area between the Cserhát and Mátra Mountains these sandstones seem to be more applicable (Figure 3, 24), although their lateral extent is probably not large enough.

The depth of this formation is also convenient in the Vatta-Maklár Trench (Figure 4, 18).

It can be decided after detailed examination (drillholes, formation water quality, impermeability of the caprock, lateral migration connections, e.t.c.) if these formations is suitable for CCS.

3.3.3. Miocene formations

The structural units of the ALCAPA and Tisza–Dacia plate blocks, which form the Palaeozoic–Mesozoic basement of Hungary arrived at their recent place in the Early Miocene. With the setting of the plate blocks, the sinking of the Carpathian Basin started.

During the Early Miocene the Egggenburgian transgression came from southeast. Due to the continuous uplift of the Carpathians rivers from north started to build the ancient deltas, indicating the early filling up of the Carpathian Basin. Along the marginal fractures of the lifting blocks, the Gyulakeszi Rhyolitic Tuff came to surface by explosive eruptions (earlier called “Lower Rhyolitic Tuff”). In the swampy marginal parts of the Ottnangian sea brown coal deposits were formed in the Nógrád and Borsod area. At the same time, in the shallow marine areas sandstone and molluscan limestone were deposited [7].

In the Middle Miocene Karpatian Age the rhyolitic explosive activity restarted (Tar Dacitic Tuff, earlier “Middle Rhyolitic Tuff”). This introduced the widespread andesitic
volcanism, which occurred in the whole Inner Carpathian Belt. In the North Hungarian basin areas sandstone was deposited. In the Badenian, the fossil-rich, shallow marine limestone (Rákos Formation, earlier “Lajta Limestone”) is widespread, but in the Nógrád area fine-grained sandstone, sandy clay, marl and silt also occur [5], [7].

In the Late Miocene the Pannonian Basin was formed. The central part of the basin started to sink intensely and the southern part of the region became a part of the Hungarian Plane. The Late Miocene is characterized by a large sedimentary cycle, with an Upper Badenian, Sarmatian and Pannonian transgressive sequence followed by regression from the end of the Pannonian. During the Sarmatian Age, the explosive rhyolitic volcanism started for the third time (Galgavölgy Rhyolitic Tuff, earlier “Upper Rhyolitic Tuff”). In the southern margins of the lifting mountains, shallow marine, porous limestone was deposited. The swampy areas started to form along the northern sea margins in the Pannonian Basin. The sedimentation was continuous until the end of the Pannonian Age [2], [7].

The Miocene sandstones can be the subject of further examinations to reveal their CCS potential. Those sandstone bodies can be taken into account, which have relatively large horizontal and vertical extent, have impermeable caprock and are situated below 800 m depth. These sandstone bodies are as follows:

- Marine Egerian-Eggenburgian sediments in the Ózd Trough (Figure 4, 27);
- Karpatian– Lower Badenian basin sediments (Figure 2, 22) and Late Miocene basin sediments (Figure 4, 19) in the area between the Cserhát Mountains and the Tura–Hatvan Blocks;
- Upper Badenian, Sarmatian and Lower Pannonian basin sediments in the Vatta–Maklár Trough (Figure 4, 27)

Figure 4: Geological cross section along line 3 in Figure 1 (After Haas et al., 2001)
3.3.4. Pannonian formations

In the Pannonian Age, which comprises the latest Miocene and the whole Pliocene (Pannonian s.l.), the Pannonian Inland Sea covered most of the Carpathian Basin. Rivers from the surrounding mountains built huge delta systems. The submerging basin was continually filled by clastic sediments, which are finally as thick as 4000–5000 m. In the Pannonian Age clastic sediments are dominant [2].

The examined area was situated in the northern margin of the basin. In the Nógrád area and the foreground of the Cserhát, Mátra and Bükk, fluvial, limnic and delta sediments were deposited, mostly sand and gravel (Borsod Gravel Formation, Edelény Formation) [5], [7].

In the Late Pannonian the inland sea margin became a limnic-swampy area, and grey-bluish gray clayey sediments were formed with inter layering lignite of maximum 15 m in thickness (Bükkalja Lignite Formation). By the end of the Pannonian the basin became completely filled up [5], [6].

As for the CCS potential, the Pannonian sandstones have good parameters. As we have to find layers deeper than 800 m, only those blocks can be considered, which were faulted down along the multiply fault systems at the mountain margins. Taking this into account we can find potential formations for CO\textsubscript{2} storage in the following areas:

- The Upper Miocene basin sediments between the Cserhát Mountains and the Tura–Hatvan Blocks (Figure 2, 27). The Upper Pannonian sandy layers (Figure 2, 28) cannot be considered because of their high position.
- In the southern foreland of the Mátra Mountains the Badenian, Sarmatian and Lower Pannonian basin sediments (Figure 3, 34) have good potential. The Upper Pannonian sediments (Figure 3, 35) can be also suitable.
- In the Vatta–Maklár Trough, the Upper Badenian, Sarmatian and Lower Pannonian basin sediments (Figure 4, 27) can be applicable if they have the impermeable sealing layers.

3.4. Quaternary formations

During the Quaternary intense vertical movements were characteristic in the Carpathian Basin. In the last 2.4 million years the mountains have emerged to 200–300 m, while the lowland areas have submerged to 150–700 m. The blocking structure is shown in Figure 3 and 4. In the Pleistocene the recent river systems were already formed, and the mountains and hills were exposed to denudation. The ancient river beds are marked by cobble horizons, and in the floodplain areas fine-grained sediments were deposited. In the southern foreland of the North Hungarian Mountains loess was accumulated [6].

Because of their high position, the Pleistocene sediments cannot be considered as CO\textsubscript{2} storage sites.

4. Conclusions: CCS potential of the examined area

Summarizing the characteristics of rock types and their position in depth, as potential formations for CO\textsubscript{2} storage the following units can be considered – if they have the suitable physical parameters and do not contain fresh water reserves:
Potential of CO₂ Geological Storage in Porous Sedimentary Formations...

- Reservoir rocks of the Mezőkeresztes–Demjén–Fedémes–Bükkszék oil fields: Triassic and Eocene fractured limestone, Oligocene sandstones and Miocene pyroclasts and sedimentary rocks,

- Marine Egerian–Eggenburgian sedimentary rocks in the Vatta–Maklár Trough (depth: 500–1000 m, thickness: 300 m).

- Miocene sandstones and sandy sedimentary rocks (depending on the depth, isolation and sealing) in the following areas:
  - The range between the Cserhát Mountains and the Tura–Hatvan blocks: The Karpathian-Lower Badenian basin sediments are at a depth of 1500–2000 m, their thickness is maximum 500 m; the Upper Miocene basin sediments are positioned between 0–1600 m depths, their thickness varies from 200 to 800 m.
  - The Vatta–Maklár Trough: Upper Badenian, Sarmatian and Lower Pannonian basin sediments positioned between 0 and 1600 m depth, their thickness varies from 500 to 1000 m.
  - Pannonian sandstones (if they have impermeable caprock) in the following areas:
    - The southern foreland of the Mátra Mountains: Lower Pannonian basin sediments at a depth between 1000–2500 m, in a thickness of 800–1500 m
    - The Vatta–Maklár Trough: Lower Pannonian basin sediments at a depth between 0–1600 m, in a thickness of 200–800 m.

Further examinations are needed on these formations in order to decide about their CCS potential. These examinations are:
- Structural geological and stratigraphic interpretation of the former geophysical data,
- Interpretation of the former drillhole documentations in the area,
- Mineralogical, petrological, geochemical and sedimentological analysis of the drillcores,
- Interpretation of the formation water quality data.

These examinations are necessary to determine the position and extent of the given formation, the physical parameters of rocks (grain size, sorting, porosity, permeability, adsorption capacity) as well as the quality of the pore fluid (excluding the fresh water reservoirs).

It is also important to clarify if there is a proper sealing by impermeable clayey rocks above the storage formation and if the formation fluid is isolated from fresh water reservoirs. To make these conditions clear several drillholes have to be carried out in the potential area.
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