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2. Brief outline of ways to store, types of CO_2 capture in a structure, capacity estimations and previous works

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During the past 250 years the combustion of fossil fuels used for power generation, heating, industry and transport has continuously increased amount of carbon dioxide emitted into the atmosphere. Almost half of the CO_2 produced by civilization is absorbed by vegetation and dissolved in the oceans. At a later period it has caused acidification of water, which has a potentially negative impact on the marine plants and animals.

The rest of the carbon dioxide has accumulated in the atmosphere. It has contributed to climate change, because CO_2 is a greenhouse gas that traps heat of the sun leading to a warming of the Earth's surface. Carbon cycle in nature is documented in Fig. 2.1.

Our research work has been focused in the methodology of the ultimate CCS chain link - the underground storage of CO_2, which is in accordance with the requirements for permanent and safe storage of critical importance.

The methodology of the storage is currently very dynamically developing sector, where actual results are primarily based on data from four repositories in which the CO_2 is stored in an industrial scale: Sleipner, Snohwit (Norway), Weyburn (Canada), and In Salah (Algeria) - www.globalccsinstitute.com. However, all these storage projects are economically tied to the production of hydrocarbons, in other words, without extracting methane deposits and enhanced extraction of oil (Weyburn) no storage would be realized. In addition, the current era can be characterized as a decade of commencement of pilot and demonstration projects. For example only in Europe in the scope of FP7 programme 12 projects were prepared covering mostly the whole CCS loop (capture from the source of emissions, through transport to disposal). *Note: Due to the crisis their number was reduced to 6.*

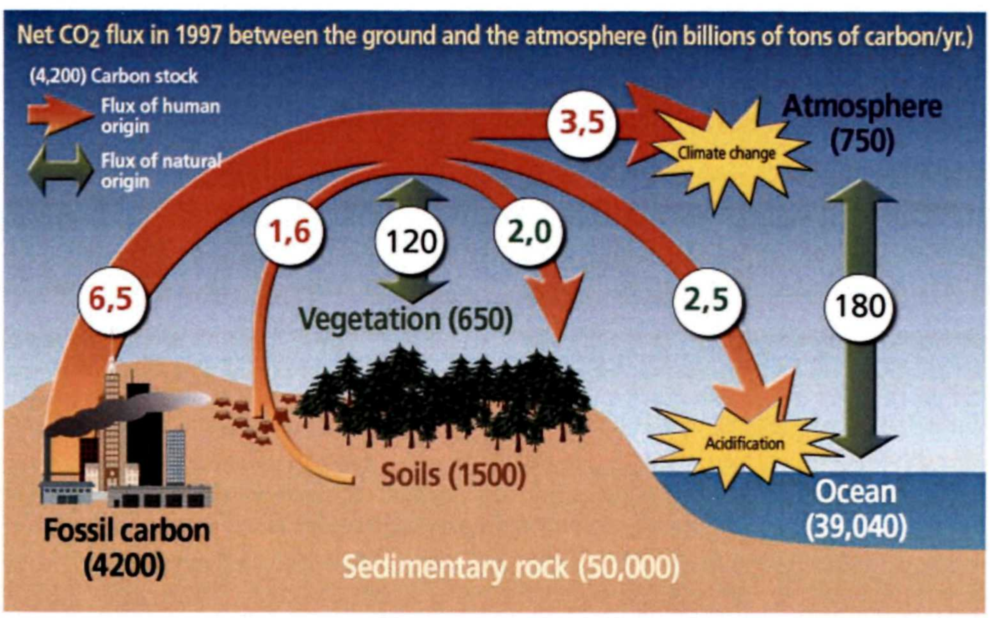

Fig. 2.1 Scheme of carbon cycle in nature (source: www CO_2 GeoNet)

The only on-shore storage in Europe is Ketzin in Germany (former gas reservoir near Berlin) with the capacity corresponding rather to field laboratory, or to a small pilot project (Liebscher et al., 2013). In the Netherlands (North Sea shelf) storage potential is examined in depleted gas reservoir (K12b) - Meer, et al., (2006). Other projects are running in Australia, Japan, USA and Canada (www.globalccsinstitute.com). Despite the fact that due to the global crisis, there has been some slowdown, mainly due to financing, the amount of professional events in the global and European scale indicates that new scientific sector has been established, which in addition to the basic problems related to CO_2 storage (geological, physical, chemical and social) adds supplementary information that may be helpful to related industries and activities. At present, according to Global Institute (Australia) across the world 74 CCS projects are integrated, of which 14 are in operation phase or under construction.

The problem of climate change is given great attention also in the western hemisphere; in the USA and Canada the third edition of the Atlas of geological structures for CO_2 storage was published. The Atlas is issued by the National Energy Technology Laboratory (NETL) supervised by the U.S. State Department of Energy (DOE). Under this initiative partnerships and consortia have been created based on the regional principle that joint efforts generating measures to mitigate the effects of global climate change

(www.netl.doe.gov/technologies/carbon.../atlasIII/).

The Slovak Republic has been a member of consortia of European projects, which elaborated initial information, estimating the theoretical storage capacities. The projects were CASTOR (Christensen, et al., 2006) and Geo Capacity (Vangkilde-Pedersen et al., 2008), coordinated by the Geological Survey of Denmark.

According to the results of the GeoCapacity project the following volumes were estimated for Slovakia (Kucharič and Kotulová, in Vankgilde-Petersen et al., 2009):

Tab. 2.1 Resuting capacities of SR for CO_2 storage (Kucharič and Kotulová, 2009)

Type of repository	Capacity	Conservative approach (Mt)	Included in database (Mt)
Regional aquifers	theoretical	1,716	13,708
Hydrocarbon deposits	theoretical	–	134
Coal seams	–	–	–
IN TOTAL		1,716	13,842

We note that according NAPL (National Allocation Plan, ME 2006) the annual output of CO_2 emissions in Slovakia is estimated at 40 Mt.

In retrospect, the aforementioned values seem to be "too optimistic". Mainly the values in the database, which reflect application of high sweep coefficient – characterizing the fill-up of the remaining (unfilled) space (pore and fissure) by gas. Its value in the formula for calculating (discussed later) was set at 40%, which in our view for the lesser studied aquifers is exaggerated. We tend to adopt the methodology proposed by May, in Chadwick et al. (2008), in which for this type of repository the sweep coefficient of less than 8%, preferably 2-4% is recommended to be used. Such an opinion we have taken into account in the "conservative approach" to estimate capacity in Slovakia. Also, the value of formation factor provided for hydrocarbon deposits is higher because we have lacked of some specific substantive inputs. This is often a problem in determining the capacity, because here we touch the sphere of private companies that keep these data protected.

In 2014, Atlas of Europe will be compiled for CO_2 storage, realized in the scope of a financially very limited project CO2Stop (Poulsen et al., 2013), based on the results of the above mentioned project GeoCapacity.

Naturally, a repository of carbon dioxide must still meet a number of parameters, of which the most important are size, hydrodynamic properties of the collector, petrographic composition and sealing of the overlying layer - its thickness and tectonic setting. Currently, there are several ways to store this greenhouse gas in various geological environments. A scheme of the storage is presented in the following figure, showing all currently accepted means of carbon dioxide sequestration. It must be emphasized that the attainment of development of techniques and technologies varies.

By comparing the means of storage shown in Fig. 2.2 it is obvious that in the present case, we did not consider the use of the non-depleted or unextractable coal seams (under current legislation the storage in the ocean is not permitted). The coal aspect we have not considered yet, because the coal seams in Slovakia are in relatively shallow depth, the coal enrichment is of low-grade and our deposits are intense tectonically disrupted, as well as their overburden.

Naturally, the gas behaviour in storage depths depends upon temperature and pressure characteristics. The dependence of gas density upon temperature and pressure parameters is shown in Fig. 2.3.

The basic characteristics of the repository are not only sufficient volume to store and the existence of an intact seal horizon in the reservoir overburden and the appropriate depth, but also optimal porosity and permeability, and coefficient of efficiency. The latter is defined as a fraction of the pore volume, currently saturated with CO_2. Of course tectonic disturbance is negative factor, and the faults should be "tightened", it means closed, or pressed by compression forces.

At a temperature of 31.1 °C and a pressure of 7.39 MPa the CO_2 gets into so-called **supercritical state** - it becomes a liquid and spreads like gas, occupies a very small volume, which is a favourable symptom for storage. This phenomenon is used for storage, where up to a depth of 800 m, the volume of gas decreases drastically. With further increasing depth the volume is not being reduced. Mainly for economic reasons the lower limit of the reservoir is considered acceptable to a depth of 3,000 m.

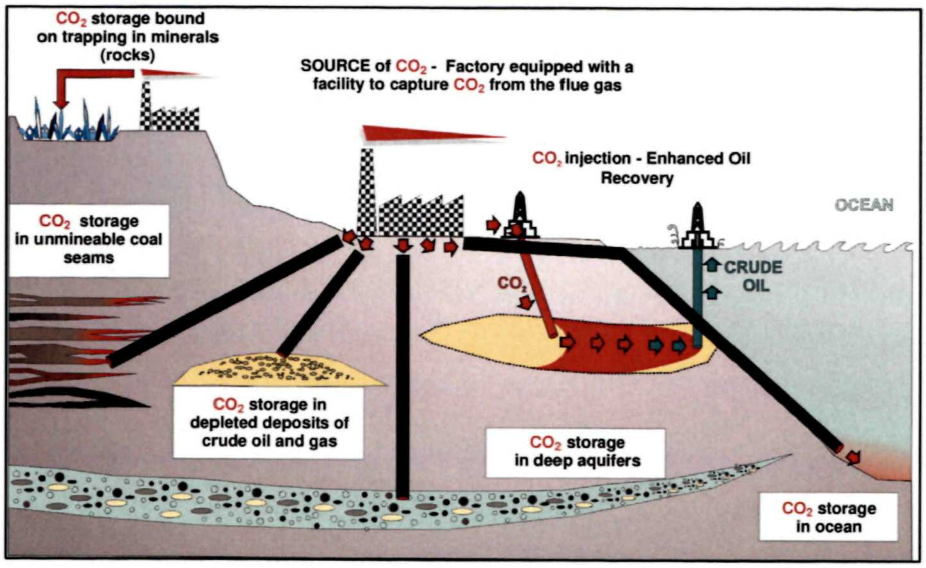

Fig. 2.2 Scheme of ways of CO_2 storage within geological environment (Kotulová in Kuchařič & Kotulová, 2007)

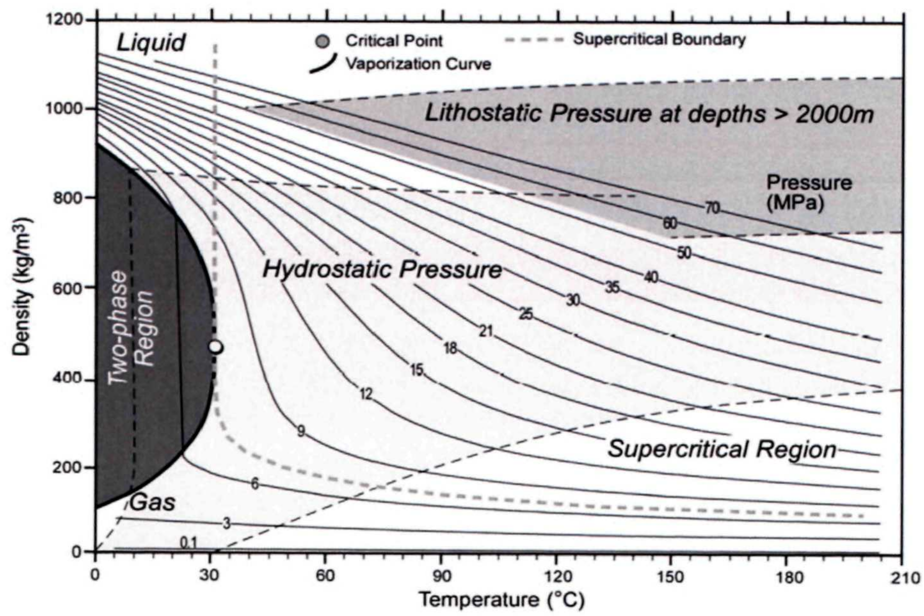

Fig. 2.3. Variation of CO_2 density with temperature and pressure, and expected range of variation in sedimentary basins (Bachu, 2006)

When storing (injecting) CO_2 into the collector the gas behaves under the following scenarios (according to CO_2GeoNet):

1. *Accumulation of CO_2 below a cap rock (structural trapping)*

As CO_2 is lighter than water, it begins to rise upwards. The movement is stopped when CO_2 encounters impermeable horizon in the roof, which prevents further upwards propagation (the cap rock). This sealing horizon is usually made of clays or salt and such cap rock acts as a trap for advancing CO_2, which causes its accumulation at the geological boundary, creating pressure on the cap rock sealing layer.

2. *CO_2 trapping in small pores (residual trapping)*

This kind of capture occurs when the pore spaces are so narrow that the CO_2 can no longer move upwards, despite the difference in density with surrounding water. This process occurs during migration of CO_2 and can immobilize (capture) a few percent of the injected CO_2, depending on the properties of collector rocks.

3. *Dissolution (dissolution trapping)*

A small proportion of injected CO_2 is dissolved or brought into solution by the brine already present in the pore spaces of the collector. A consequence of dissolution is that the water with dissolved CO_2 is heavier than the

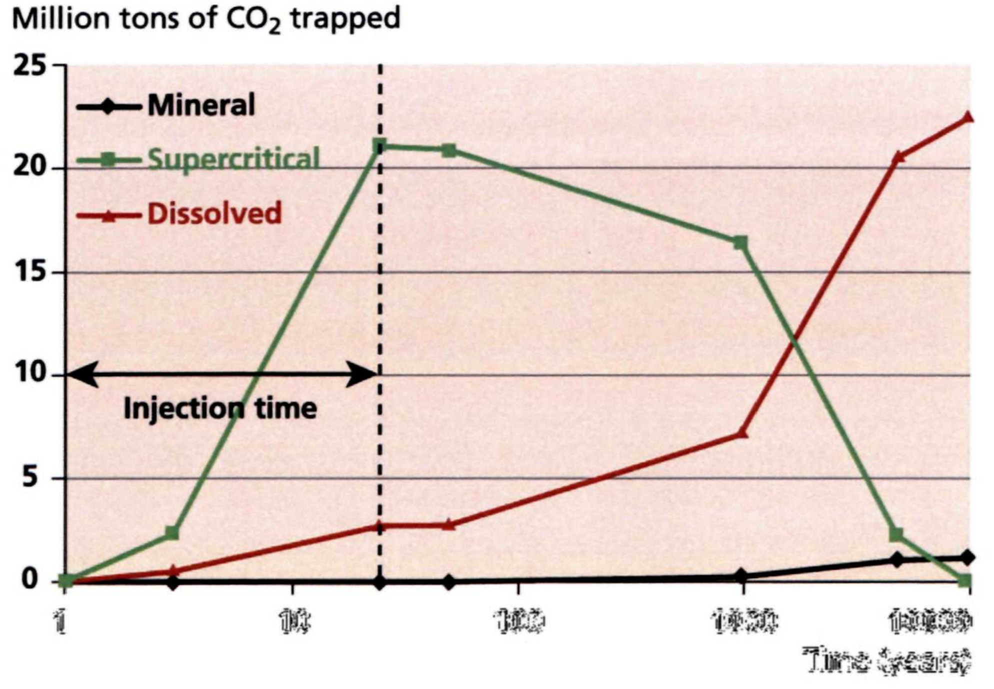

Fig. 2.4 Behaviour of CO_2 at Sleipner reservoir, Norwegian sea (source www. CO_2GeoNet)

original water in the collector. This causes its downward migration to the bottom of the collector (reservoir). The intensity of dissolution depends on the contact between CO_2 and saltwater. The amount of CO_2 that can be dissolved is limited by a maximum concentration. However, due to the moving of injected CO_2 upwards and the water with dissolved CO_2 downwards there is a continuous renewal of the contact between CO_2 and brine. This has the effect of increasing the amount of CO_2 that can dissolve within. These processes are relatively slow because they take place in narrow pore spaces. Approximate estimates at the repository Sleipner (Norwegian Sea) indicate that approximately 15% of the injected CO_2 is dissolved after 10 years of injection.

4. *Mineralization (mineral trapping, mineral carbonatization)*

The CO_2, especially in combination with the brine in the reservoir, may react with minerals actually forming the rock. Certain minerals may dissolve and some of them precipitate, depending on the degree of pH and the minerals constituting the reservoir rock.

Estimates at Sleipner (Norway) indicate that only a small amount of CO_2 is captured through mineralization over a very long period of time. After 10,000 years, only 5% of the injected CO_2 should be mineralized, while 95% would be dissolved without residue, with no CO_2 remaining as a separate dense phase migrates towards the surface (Fig. 2.5, light blue bubbles), dissolves rock grains and responds to them. This leads to the precipitation of carbonate minerals on the surface of grains (white edges). Relative importance of these trapping mechanisms is specific for each reservoir, it means, it depends on the characteristics of each site. For example, in a dome-shaped structure the CO_2 should remain mostly in a dense phase even over a long time, while in flat repositories the most of the CO_2 is mostly dissolved.

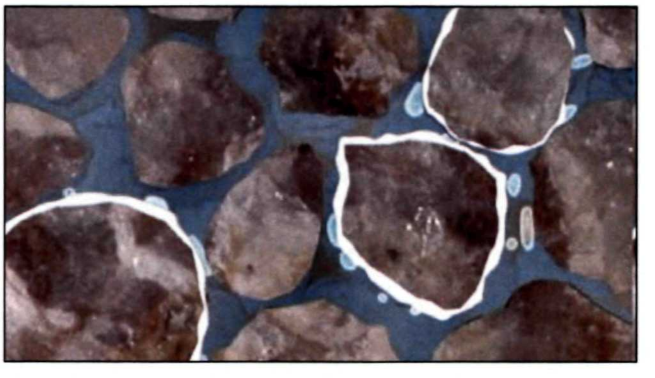

Fig. 2.5 Dense CO_2 migrating upwards (light blue bubbles), dissolving and reacting with the grains of the rocks. Leading to precipitation of carbonate minerals on the grain boundaries (white). (Source CO_2GeoNet).

Behaviour of CO_2 in various forms of trapping (see points 1-4), based on the results of the modelling and storage at Sleipner is documented in Fig. 2.4.

From the above it follows, that the type of trapping plays a significant role in site selection, yet over long time periods (thousands of years) there should be a gradual reduction in pressure in the dome, or sealing part of a structure. This means, the increasing proportion of the types of trapping by mechanisms 2-4 would occur. And that is essentially the basic postulate to achieve safe disposal of the gas.

Variable geological setting offers the same variable number of suitable types of reservoirs. It is clear that during exploration and research work on the selected type of storage, single positive or less favourable criteria will vary depending on the detail of the information obtained. Therefore, it is quite difficult to define the exact parameters that must have a repository, but still certain interval endpoints can be delineated, which should be respected.

The table above represents only a summary of the basic attributes, collected from a variety of sources, according to which the selection of suitable sites for underground storage could be realized. It is not possible to create an universal formula, reflecting all possible cases, because the geological situation of each object is unique even within a single lithostratigraphic unit and weight of individual parameters may be different in each case. The final output of a repository exploration should calculate the storage capacity. Mainly for regional aquifers, this calculation will differ significantly from reality whatever correction we would use, as in the calculation "estimates of averaged" values have to be included. For the calculation of capacity in regional aquifers a formula was used (Brook, 2003):

Tab. 2. 2 Indicators for convenient type of reservoir

	Positive indicators	Warning indicators
Overall reservoir capacity	Estimated capacity much greater, as an overall amount of CO_2 emitted from a source	Estimated capacity roughly the same, as an overall amount of CO_2 emitted from a source
	Depending upon a source in question, calculated capacity sufficient for a time span over 20-30 and more years	Depending upon a source in question, calculated capacity sufficient for a time span of 10-15 years
Reservoir properties		
Depth	>1,000 m <2,500 m	<800 m >2,500 m
Thickness	>50 m	<20 m
Homogeneity and anisotropy	Homogeneity high, anisotropy low	Homogeneity low, anisotropy high
Porosity	>20%	<10%
Permeability	>300 mD	<10-100 mD
Salinity	>100 $g.l^{-1}$	<30 $g.l^{-1}$
Properties of cap rock		
Horizontal relation	Without faults	Horizontal inhomogeneity, tectonic failures
Thickness	>100 m	<20 m
Input capillary pressure	Input capillary pressure much higher than heave force of the assumed CO_2 column height	Input capillary pressure similar to heave force of the assumed CO_2 column height

$$\mathbf{M = S \times h \times p \times \varsigma \times F}$$

where

M – CO_2 storage capacity Mt (million) tonnes

S – aquifer area

h – thickness

p – porosity

ς – density in given depth

F – sweep coefficient

There are at hand many other relationships and methodological approaches. In our opinion, however, at this stage, the above formula is sufficient, especially if we consider a variability of physical and chemical parameters in the "Carpathian conditions". With the current knowledge of the structures of interest by introducing more complex patterns we would receive "accurate results" using inaccurate (often estimated) input data. Chemical parameters in this case are not taken into account, but in the case of storage they are crucial for the behaviour of CO_2 in the reservoir.

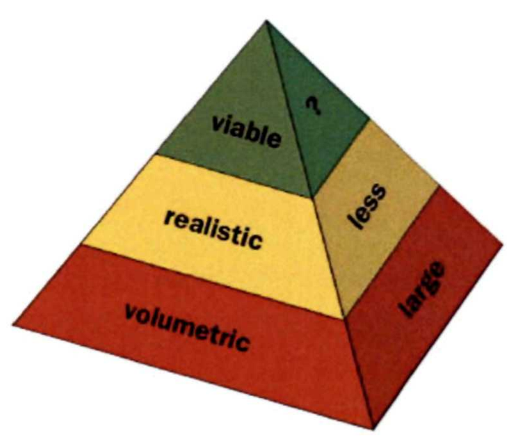

Fig. 2.6 Pyramid expressing calculation of storage capacity

Due to the fact that we are not really capable, especially in aquifer objects, to assess realistically the behaviour of certain parameters, or to replace the missing values by the principle of analogy. We are forced to introduce the so-called expert estimates, and the resulting calculated capacity must be taken as educated guesses. In the capacity assessment a classification by Bradshaw, et al., (2007) has been adopted, where each capacity level represents a pyramid, based on the concept of techno-economic repository pyramid, which reflects the degree of uncertainty, along with economic viability, coupled with the capacity estimation. In principle, this means that by growing work, namely the acquisition of results calculated capacity gradually decreases (see Fig. 2.6).

In the case of depleted hydrocarbon deposits, the situation is simpler, actually more realistic because we have enough reliable data on exploitation not only in terms of capacity, but also deposit tightness, pressure, temperature, residual stocks, etc. ....

In the scope of the project GeoCapacity the following formula was used (Schuppers, 2006):

$$\mathbf{M = \varsigma \; x \; U_{RB} \; x \; B}$$

where

M CO_2 storage capacity

ς CO_2 density

$\mathbf{U_{RB}}$ proven ultimate recoverable volume

B formation volume factor for gas (oil)

Our calculation for hydrocarbon deposits is dealed with in the next chapter.