POTENTIAL, CAPACITIES ESTIMATION AND LEGISLATION FOR CO$_2$ STORAGE IN THE GEOLOGICAL FORMATIONS OF THE SLOVAK REPUBLIC

Editor: Ľudovít Kucharič

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Instructions to authors

General instructions

The Editorial Board of the Slovak Geological Magazine accepts manuscripts in English language.

The Editorial Board accepts or refuses a manuscript with regard to the reviewers` opinions. The authors are informed about a refusal within 14 days after receiving the decision of the Editorial Board. Accepted manuscripts are prepared for a publication in an appropriate issue of the magazine. The author(s) and the publishers enter a contract establishing the rights and duties of both parties during editorial preparation and printing, until the time of a paper publishing. Simultaneously with article the editorial office must receive the corresponding author's proclamation that no part of the manuscript was already published and figures are original as well. Copied figures must be legalized by obtaining the copyright. The proclamation must contain the name of author (authors), title and the address of residence.

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The text should be arranged as follows: full name of the author(s); title of the paper, number of supplements (in brackets, below the title, e.g. 5 figs., 4 tabs.); key words - maximum 6 key words arranged successively from general to special terms; abstract (max. 300 words presenting principal results, without references); in a footnote of the first page, name of the author(s) as well as her/his/their professional or private address.

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Mathematical and physical symbols of units, such as m, °C should be preceded by a space, e.g. 20 m, 50 °C, etc. In the case of % and ‰, the exemption shall be made: 10%, 2‰. SI units are preferred. Abbreviations of the units such as second, liter, etc. should be written without a period. Compass readings may be substitute by the abbreviations E, W, NW, SSE, etc. Brackets (parentheses) are to be indicated as should be printed, i.e. square brackets, parentheses or compound. Dashes should be typed as double hyphens.

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Photographs must be sharp, preferably black & white, contrast, in the form of JPG or TIFF files having resolution of at least 600 DPI.

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Book

Gazda L. & Čech M., 1988: Paleozoic of the Medzev nappe. Bratislava, Alfa, 155.

Journal

Vrba P., 1989: Shear zones in the metapelite complexes. Mineralia Slov., 21, 135-142.

Anniversary volume

Návesný D., 1987: High-potassium rhyolites. In: Romanov, V. (ed.): Stratiform deposits of Gemericum. Spec. publ. Slov. Geol. Soc. Košice, 203-215.

Manuscript

Radvanský F., Slivka B., Viktor J. & Srnka T., 1985: Vein deposits of the Jeďovec nappe of Gemericum. Final report from the project SGR-geophysics. Manuscript-archive ŠGÚDŠ Spišská Nová Ves, 28.

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The manuscripts should be sent by e-mail to the address: slovak.geological.magazine[at]geology.sk.

POTENTIAL, CAPACITIES ESTIMATION AND LEGISLATION FOR CO$_2$ STORAGE IN THE GEOLOGICAL FORMATIONS OF THE SLOVAK REPUBLIC

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Foreword

Climate change poses the biggest threat facing today's society, with the exception of global military conflicts. Its negative effects are almost universally felt in everyday life and the fact has been accepted that global warming is directly related to the civilisation activities linked with the production of energy, which is an indispensable means to ensure the socio-economic development of the society. The upward trend in energy consumption in the developed countries and the provision of basic energy needs in developing countries in the context of the continuous growth of the world's population, requires a permanent increase in the energy production. This is covered almost 85% by the burning of fossil fuels, producing a greenhouse gas – carbon dioxide, which is considered to be the main component of global warming. Our civilization is challenging the fundamental solution of the problem: finding ways how to satisfy the energy demands of the society while maintaining or even reducing the CO_2 concentration in the atmosphere. It is therefore logical that global efforts are heading for to minimize the production of CO_2 in the world. To achieve this goal there are currently accepted and supported the following activities: first of all, an enhanced efficiency in energy production, in keeping with the austerity measures in the management of its use. The next is an effort to increase the share of renewable energy in its production, and finally the underground CO_2 storage technology, it means into its original environment (Carbon Capture and Storage - CCS). The Slovak Republic by means of the project "Quantitative Parameters of Geological Structures Suitable for CO_2 Storage," financed from the resources of the Ministry of Environment (MoE SR) has been engaged in a global effort to identify suitable geological structures in which the greenhouse gas should be permanently and safely stored. Partial results of the task being completed in the course of its solutions were presented on a wide range of national, European and worldwide events in the form of presentations, posters, as well as publications in national and foreign journals. This publication offers a brief summary, presenting the results of the above tasks, as well as accompanying activities, such as the creation of the necessary legal instruments in European and Slovak area, covering the activities of the CCS. In this work are outlined capacity and possible ways for underground CO_2 storage. On the basis of its results it cannot be initialized immediate implementation of the gas storage into a repository; it will require more detailed work, but its main objective has been to direct targeted activities related to CCS within the territory of the Slovak Republic in such rock structures that are potentially the most suitable for this purpose, if the global situation in the field of CO_2 emissions in the future period would ask for.

Ľudovít Kucharič

Abstract

This monograph presents a summary evaluation of potential CO_2 storage options in Slovakia under current state of knowledge. We have assessed depleted hydrocarbon deposits, local and regional aquifers and selected basic and ultrabasic bodies, in order to estimate their potential capacity. Selected aquifers were modelled geochemically using PHREEQC code. The research has shown that in spite of a sufficient quantity of relevant data the hydrocarbon deposits are not suitable for industrial storage due to their limited storage capacity (<10 Mt); however they meet criteria for a pilot project. The only exception is gas deposit Vysoká - Zwerndorf, which is shared by Slovakia and Austria. Local and regional aquifers present significantly larger structures but their estimated capacity is only theoretical, because in the vast majority of cases representative data are missing. Mineral carbonatization was carried out by ex situ technology in a laboratory scale, using high-pressure reactor PARR 4540. We have evaluated selected ultramafic and mafic bodies. The results were confronted with petrological calculations of data obtained on electron microanalyzer CAMECA SX 100. Calculated and estimated capacities of individual structures were inserted into relevant databases. We provided a description of a legislative framework delimiting the activities in question. A list of sites from around the world is attached, along with the relevant data, at which CO_2 is stored, or considered for storage. This allows to create a global perception of the technological development in the near term.

Key words: Slovak Republic, CO_2 storage, depleted hydrocarbon deposits, local and regional aquifers, estimation of storage capacities, geochemical modelling, mineral carbonatization, legislation.

Acronyms and symbols

ASTM	tables
CASTOR	CO_2 from capture to storage**.** EU project – the 6-th FP
CCS	Carbon Capture and Storage
CGS Europe	the Pan-European coordination action on CO_2 Geological Storage EU project – 7-th FP
CHA	Chemical Silicate Analysis
CO_2GeoNet	The European Network of Excellence on the Geological Storage of CO_2
CO2Stop	Assessment o f CO_2 storage potential in Europe. Specific Targeted Research Project
ČND	Československé naftové doly (former research and extraction company)
DOE	U.S. State Department of Energy
DTA	Differential Thermic Analysis
DTG	Differential Thermogravimetric Analysis
EC	European Commission
EGR	Enhanced Gas Recovery
ENGAS sro	Slovak private extraction company
EOR	Enhanced Oil Recovery
EP	European Parliament
EU	European Union
FP 6 EU	the 6th Framework Programme
FP 7 EU	the 7th Framework Programme
GeoCapacity	Assessing European Capacity for Geological Storage of Carbon Dioxide EU project – 6-th FP
IKŽ MZ SR	Inšpektorát Kúpeľov a Žriediel Ministerstva zdravotníctva Slovenskej republiky - Inspectorate of Spas and Springs of the Ministry of Health SR
IPCC	Intergovernmental Panel for Climate Change
UNFCC	United Nations Framework Convention for Climate Change
MŽP SR/MoE SR	Ministry of Environment of the Slovak Republic
NAPL	National Allocation Plan for years 2008 – 2012 to Directive 2003/87/EC
NETL	National Energy Technology Laboratory
OGIP	Original Gas In Place
OOIP	Original Oil In Place
ÖMV	Österreichische Mineralölverwaltung
PHREEQC	code for hydrochemical modeling
UGSF	Underground Gas Storage Facility
RTG	X ray diffraction analysis

1. Introduction

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In the last decade the issue of climate change (global warming) has become extremely current and is an integral agenda for the highest executive authorities in virtually every developed and developing countries. According to the latest report of the Intergovernmental Panel on Climate Change – IPCC (2007), the increasing CO_2 concentration in the atmosphere, causing global change, is accountable to our civilization with its rising energy demands. In the period of nearly 10 000 years preceding the industrial revolution, a balanced cycle of a natural exchange of carbon between the atmosphere, oceans, biosphere, geosphere, had supplied concentrations of CO_2 in the atmosphere at a level of about 280 parts per million, i.e. 0.028%. Over the last 250 years, which can be called an industrial era, excessive burning of fossil fuels for power generation, heating, industry and transport has increased continuously the quantities of carbon dioxide emitted into the atmosphere. Almost half of the CO_2 produced by civilization was absorbed by vegetation and dissolved in the oceans. At a later stage it caused the acidification of waters, which has had a potentially negative impact on marine plants and animals. The rest of the carbon dioxide accumulated in the atmosphere. Thus, it has contributed to the climate change, because CO_2 is a greenhouse gas, that captures a portion of the heat of the Sun and causes warming of the Earth's surface. Ultimate requirement of the UNFCCC (United Nations Framework Convention for Climate Change) is to stabilise greenhouse gas concentration at a level that would prevent dangerous anthropogenic impact on the climate. Immediate radical action is therefore necessary, which would reduce the current concentration of CO_2 reaching 387 ppm (which is about 38% more than the concentration in pre-industrial era) and so prevent the increase in the upcoming decade on a critical level of 450 ppm, which represents an increase of the average temperature on 2°C. Exceeding this threshold would mean inability to avert dramatic consequences of the warming of the planet.

Geological storage of carbon dioxide (CCS-Carbon Capture and Storage) is one of the ways to contribute to the efforts to keep the concentration of CO_2 in the atmosphere at the desired level, on the basis of the inherent premise - to bring back the carbon dioxide there, from where it was actually extracted - into the underground geological objects. By issuing a **Directive on the geological storage of carbon dioxide** (2009/31/EC) in 2009 the European Union as one of the leaders of the scientific research in this field, developed a legislative framework for these activities with the subsequent bundling of industrial activities. Its transposition into national legislations in the territory of the Slovak Republic is secured by the Act **No. 258/2011 Coll.** (Act on the Permanent Storage of Carbon Dioxide in Geological Environment and on Amendments to further laws), which entered into force on the date of issue, 12.7. 2011. This act strictly defines and sets out the activities and related issues linked to the technology.

This publication presents the relevant results of the project of the MoE SR "Quantitative parameters of selected rock structures suitable for CO_2 storage". It outlines selected geological objects across the territory of Slovakia, which might serve the purpose. We have to note, that the project was launched in 2007, this means prior to aforementioned Directive and Act came into force. This could lead to a false conclusion that there arise conflict of interest in those activities, which have been stated in § 3 section 3 of the innovated Act - storage of hydrocarbons, radioactive and other waste disposal, eventually geothermal energy utilization. The fact is, that the derived legislation is being developed. In Europe the period of pilot projects has been launched and the expected results will for sure lead to an update of the Act. Of the same importance is also the medium-term factor, in which a change in the triangle gas recipient – waste disposal (CO_2 included) – geothermal energy, is envisaged. A proof for this is the fact that in USA the CO_2 agenda has got in the forefront, accounting for its possible utilisation in geothermal energy production (Pruess, 2006, Saar, et al., 2010, Randolph and Saar, 2011, Buscheck, et al., 2013).

The level of the objects elaboration varies, depending on the works carried out so far, mostly for other purposes (raw materials, geothermal, hydrogeological, ...), therefore, we had to adopt the data, which originally had not been retrieved for this purpose. Certainly not all the possibilities have been exhausted in the choice of objects, which varied geological structure of our territory has to offer. This is linked with the fact that the data from the larger depths that the issue needs are not sufficiently precise and in such quantity, which would serve to solve the problem. In addition to focusing on the objects that
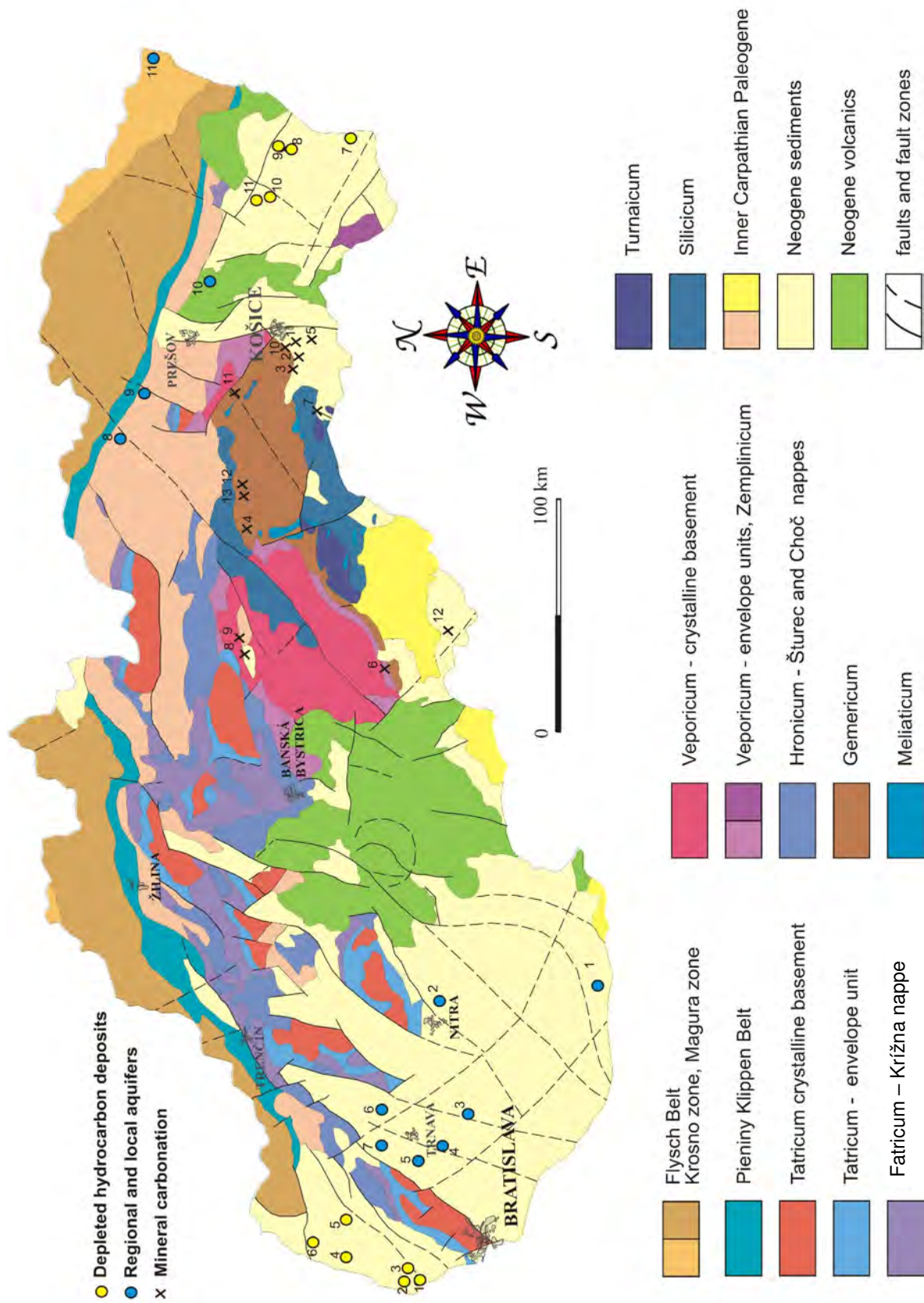
Fig. 1.1 Scheme of geological structures evaluated for the potential CO$_2$ storage (Simplified geological map – source Biely et al., 2006)

fall under the scope of problematics newly defined in the Act (extracted hydrocarbon deposits and regional aquifers), there are also options for storage, which have not yet reached a *stage of maturity*, but their scientific results are positively reflected not only in this area, but also in raw minerals technology (mineral carbonatization).

We would like to stress that we have looked at purely physico-chemical parameters, i.e. we did not take into account neither socio-economic factors that are crucial in such cases nor the share of an object with the neighbouring countries, which could also be considered. The CCS is understood as an integral part of the global energy agenda. Roadmap for the EU's energy is set out to a horizon 2050, and according to different scenarios CCS participation is close to 30%. So if there will not happen a sudden change either in the attitude of the scientific community on this issue, accounting for trends in CO_2 emissions, or in the top executive management attitude, the problem will be current at least for one generation.

The main objective of the project was to point out the possibilities of carbon dioxide storage in appropriate geological structures, taking into account their quantitative parameters, in order to reduce its concentration in the atmosphere, and to outline the potential of the Slovak Republic territory which may contribute to the global effort to minimize the adverse effects of global climate change. On the basis of current knowledge of the geological setting of the territory of the Slovak Republic, in particular, and of the knowledge-based global economy the task was solved in two basic lines (1. and 2.):

1. To determine the potential for carbon dioxide storing in appropriate water-bearing* structures

1.1. The extracted hydrocarbons spaces in the productive areas of Slovakia (Palaeogene, Neogene)

1.2. Regional aquifers of Tertiary complexes - Flysch, Palaeogene, sedimentary Neogene and volcanites

2. Potential for carbon dioxide storing in the appropriate rock complexes - mineral carbonatization

2.1. Ultramafic and mafic rocks.

Note:*Please note that attention was paid to the structures that contain salt water, i.e. the water that is not suitable for the supply of the population for drinking purposes.

For the purpose of CO_2 storage our effort has been concentrated in the following sites – Fig. 1-1:

- Depleted hydrocarbon deposits - Vysoká – Zwerndorf, 2. Jakubov, 3. Láb, 4. Závod, Mesozoic, 5. Studienka, Závod, 6. Gbely, 7. Ptrukša, 8. Stretava, 9. Senné, 10. Bánovce, 11. Trhovište- Pozdišovce.
- Regional and local aquifers - 1. Marcelová, 2. Ivánka – Golianovo, 3. Sereď, 4. Cífer, 5. Báhoň, 6. Trakovice, 7. Krupá, 8. Plavnica, 9. Lipany, 10. Zlatá Baňa, 11. Zboj.

- Mineral carbonatization - 1. Hodkovce, 2. Rudník, 3. Jasov, 4. Dobšiná 5. Komárovce 6. Breznička, 7. Miglinc, 8, Filipovo, 9. Beňuš, 10. Semša, 11. Jaklovce, 12. Bulhary.

The task of the works at the extracted hydrocarbon deposits was to collect the relevant data retrieved during the mining activities and to assess the selected sites for the purpose of storing with particular focus in the capacity and the safety aspect.

Similarly, in the regional aquifers the goal was to try to test and outline the capacity of selected sites on the basis of geological works, which were at disposal, even though it was obvious that in this case we had to introduce a number of so called expert estimates, mainly because relevant data were not available.

The main aim of the geochemical works was to highlight the geochemical and hydrogeochemical issues associated with the storage of carbon dioxide in appropriate geological structures - collectors of the groundwater. The issue takes into account quantitative and qualitative parameters, which can be reviewed on the basis of the existing hydrogeochemical and hydrogeological documentation and experimental verification of the possibility of carbon dioxide injecting. In this respect, the most important tool is simulation of geochemical processes in the course of CO_2-water-rock interactions using mathematical modelling, as well as the natural water genesis within particular hydrogeological structure.

The main objective of the technological part of the geological task was to point out the possibility of carbon dioxide storing (CO_2) into suitable geological structures, or to demonstrate CO_2 geological sequestration (disposal) using selected materials from specific sites in Slovakia in a way of mineral sequestration. All the methodological procedure was realized ex-situ - this means by sampling in the field and testing in laboratory reactor. In the implementation of the experimental research work, we simulated the P-T-t parameters (pressure, temperature, time) under laboratory conditions to determine the options and the potential to store CO_2 via method of mineral carbonatization in convenient lithologic complexes.

The aim of the petrolological works was to verify experimentally the Western Carpathians ultramafic and mafic rocks useability for industrial storage (CO_2 industrial emissions captured through their carbonatization, as well as to inspect the newly created artificial synthetic minerals).

The results of all the above works served to estimate the storage capacity of individual sites with their quantification and sorting in the database.

Notice: The Fig. 1.1 presents all the investigated sites in the framework of the project (Kucharič, et al., 2011), however in the text of this monograph are described the sites with the closest practical usage based on their identified parameters.

2. Brief outline of ways to store, types of CO₂ 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.*
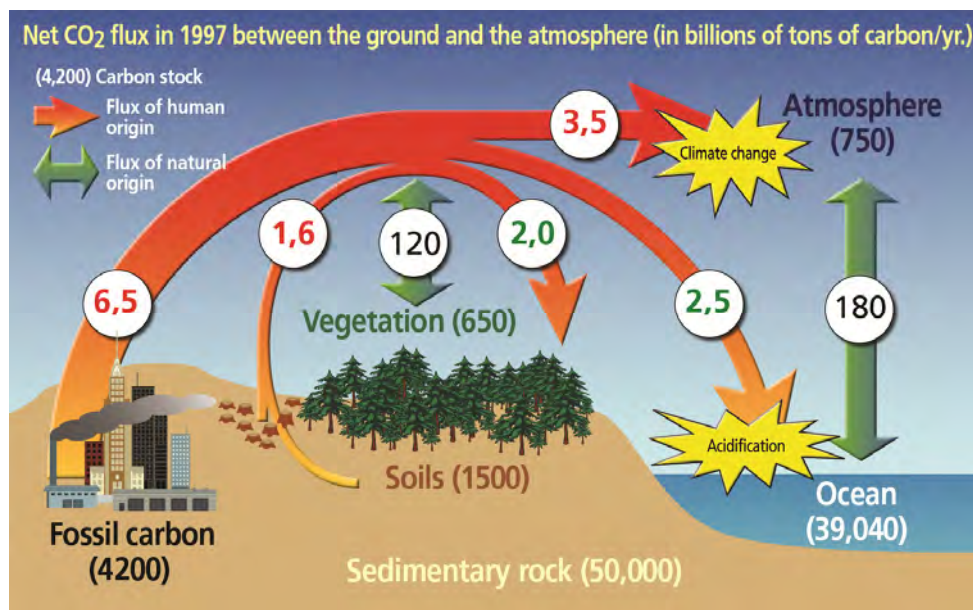
Fig. 2.1 Scheme of carbon cycle in nature (source: www CO₂ GeoNet)

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 $^\circ$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.
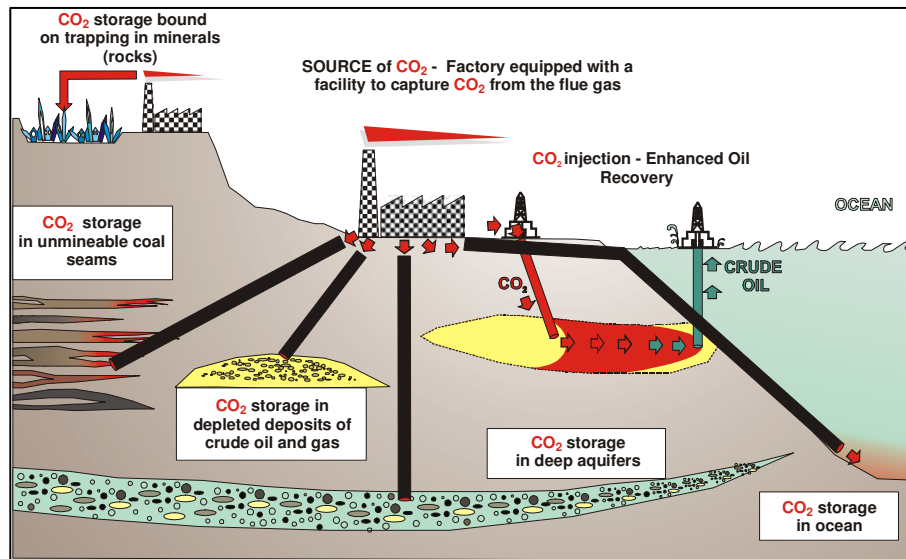
Fig. 2.2 Scheme of ways of CO_2 storage within geological environment (Kotulová in Kucharič & Kotulová, 2007)
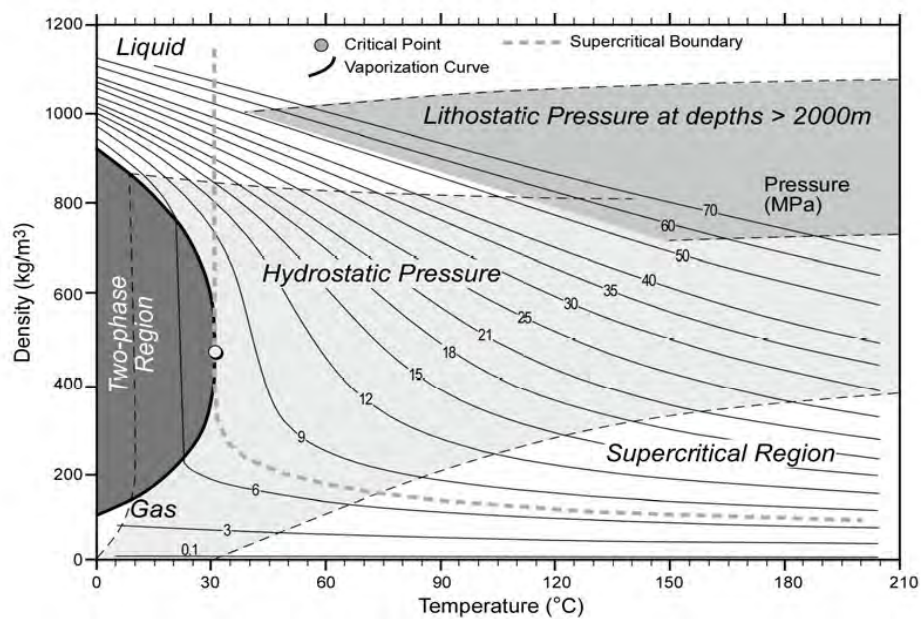
Fig. 2.3. Variation of CO_2 density with temperature and pressure, and expected range of variation in sedimentary basins (Bachu, 2006)

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
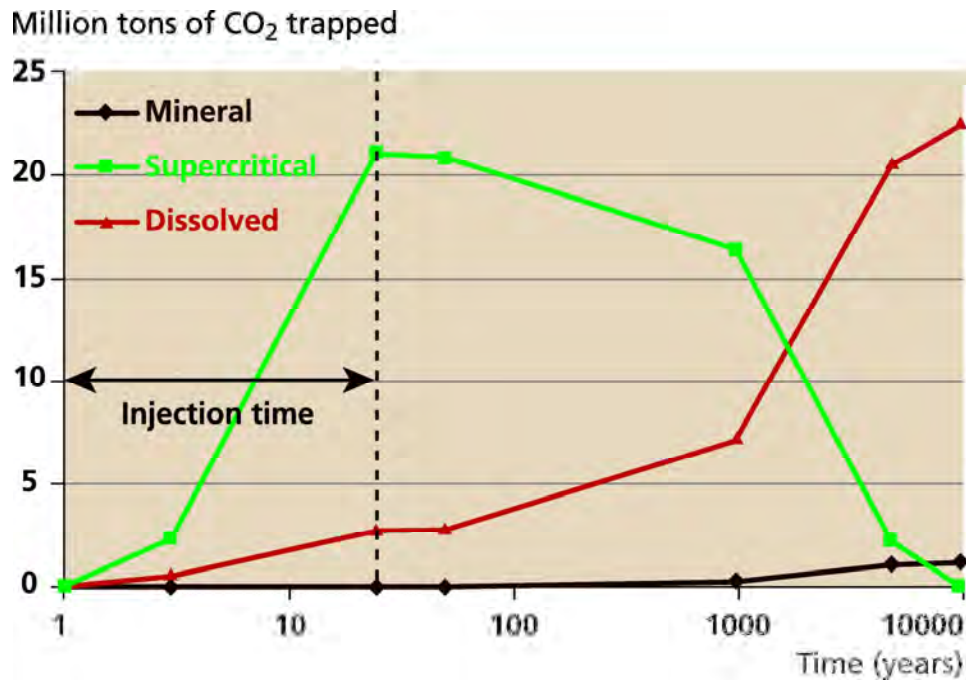
Fig. 2.4 Behaviour of CO₂ at Sleipner reservoir, Norwegian sea (source www. CO₂GeoNet)

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

Fig. 2.5 Dense CO₂ 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 CO₂GeoNet).

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.

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

$$M = S \times h \times p \times \varsigma \times F$$

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.
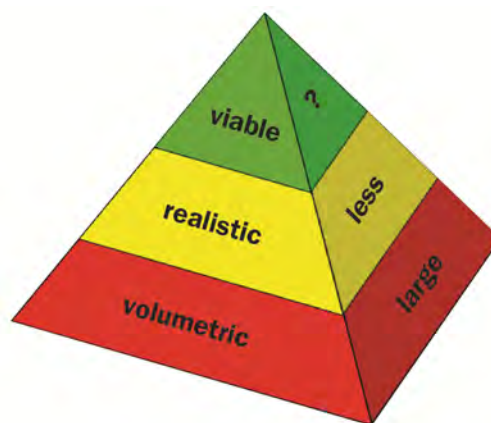
Fig. 2.6 Pyramid expressing calculation of storage capacity

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 in-

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troduce 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):

$$M = \varsigma \times U_{RB} \times B$$

where

M CO_2 storage capacity

ς CO_2 density

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.

3. Depleted hydrocarbon deposits

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3.1 Depleted hydrocarbon hydrocarbon deposits in Vienna and East Slovakian Basins

The capacity of the reservoirs of oil and gas for this review are defined as underground volumes that had been carriers of natural oil or natural gas, which, in the future - can be used to store carbon dioxide. In these cases it is not necessary to inspect the sealing of the original structures (the spill points), because the sealing of these structures and hydrocarbon reserves (determined either by the volumetric method, or the method of decrease in pressure) has been confirmed by extracted volume. In the calculation of carbon dioxide storage capacity we disposed exclusively with the original lithological conditions, that is, in the case of not exceeding the value of the original deposit pressure pressure values of each object, which is the main justification for the retention of stored CO_2, and in the careful progress of security minimising the risk of deposit capacity of spill through the cap.

The existence of the hydrocarbon accumulation is also a testament to the original system had not been suitable as potable water source and therefore there is no secondary threat to the sources of drinking water.

The hydrocarbon production demonstrated that porous space is communicative, i.e. if we are talking about its volume, it is the volume of the effective porosity and its permeabilities are conducive for the flow of media and the deposit circumstances might be favorable even in the reverse deposit operation, i.e. during the injection and storage of carbon dioxide in these depleted spaces. In many cases, the deposit pressure after extracting the original hydrocarbon reserves is substantially lower than the value of the original pressure and this pressure difference can be understood as a value representing a potential volume, which could be replaced by a stored carbon dioxide. The methodology for calculating the storage volume for deposits of oil and/or natural gas have been simplified in order to provide the broadest possible applicable basis (the source of the U.S. Department of Energy, 2006).

The calculation was based on the quantification of the CO_2 volume, where both the hydrocarbons volume and the CO_2 volume are calculated according to the original terms and conditions, in which the accumulation of hydrocarbons had existed in the original deposit. Two basic methods are used for the evaluation: (a) the volumetric calculation of the stored CO_2 capacity and (i) the calculation of original production of hydrocarbons in order to determine the capacity of the stored CO_2. Key data used such a value that better suits the existing data (if there was a production of deposit/deposit object/part of deposit object, the (ii) methodology was used. In both methodologies the efficiency of the use of the original pore volume is reflected.

(i) Volumetric calculation of geological objects storage capacity for CO_2 storing using the standard methods for calculating the initial volume of geological oil reserves (OOIP) and the original volume of the geological reserves of natural gas (OGIP) - it is determined by the "coefficient of effective use of original volume" – "E" (as a fraction of the original total capacity of pore space):

$$G_{CO_2} = V.\phi.(1-S_w).B_i.\rho.E\,,$$

For the calculation of the formation factor B_{gi} we used the Standing`s formula:

$$B_{gi} = \frac{P_s \times T_f}{P_{fi} \times T_s} \times Z_{fi}$$

P_s, P_{fi} - standard pressure, the initial deposit pressure (MPa)
T_s, T_f - standard temperature, temperature of a deposit (K)
Z_{fi} - compressibility coefficient of gas under the conditions of the T_f and P_{fi}
The value of standard pressure is 0.1013 MPa
The value of standard temperature is 293.2 K (20 ℃)
Basic data entering into the calculation are listed in the individual sheet forms of the deposit objects.

(ii) Calculation of geological objects storage capacity for CO_2 storing based on the original production makes use of the standard methods for calculating the initial volume of geological reserves of oil (OOIP) and the original volume of geological reserves of natural gas (OGIP), taking into account the fact that the volume of the produced hydrocarbons is known.

The volume of produced hydrocarbons corresponds to (a) the effective volume of rocks, (b) the value of the effective porosity of the rock – through their multiplication we shall get effective pore space, (c) saturation with hy-

drocarbons – effective pore space filled with hydrocarbons, and (d) the coefficient of factual mining exploitability R_f is determined by the ratio of the achieved extraction vs the original volume of geological reserves of hydrocarbons (in the case of non-extracted deposit the coefficient is determined from the reserves calculation). In this way, we get the value of the extracted volume of hydrocarbons registered at the surface:

$$Q_{CH} = \frac{V.\phi.(1-S_w)}{R_f}$$

Then to calculate the storage capacity for the given storage conditions we use a relationship, in which we convert the volume of extracted hydrocarbons measured at the surface by means of formation factor B_i to the volume in the original geological conditions and for this volume we determine the CO_2 storage capacity by using the value of the density of CO_2 storage in such conditions, which are known for the given object:

$$G_{CO2} = Q_{CH}.B_i.\rho \; .$$

This method is applicable in the circumstances, that there are reliable records of the course of mineral extraction. The extracted deposit water volumes and volumes of the accompanying raw materials (especially gasoline when extracting natural gas and dissolved gas in oil) are not taken into account in the calculations in ordinary cases. As well, in this calculation the volumes of injected water are not comprised, although these data ought to be included into the detailed analysis for the specification of the given projects.

In the application of this methodology, it is important to use the appropriate formation factor, in order to implement properly the conversion of hydrocarbons volume registered at the surface in relation to the volume which the original raw material occupied in deposit conditions.

The conversion of geological reserves of oil and gas

For the calculation of the capacity of the deposit objects that have been previously saturated with oil, the values of the oil density have been used according to laboratory analyses of local samples.

Assessment of the suitability of the objects and their evaluation

Another part of the handling the set of the data describing basic geological, deposit, security, capacity and relational links between the sources of emissions and their disposal sites, represent the analysis, suitability assessment and evaluation of each documented object. This procedure is designed in such a sequence and the structure of the record, which allows to compare relative usefulness of objects included in the outline.

Evaluation of objects is designed in groups of data, which are both subject to verbal description of the facts and at the same time, a classification scale is proposed for various arguments.

The assessment covers the categories of:
1. Suitability of assessed deposit structure
2. Reliability of the verification and the description of the geological circumstances of the deposit structure
3. The conflicts of interests with other mining activities
4. Threats, which may pose in the long term the use of the deposit structure.

Each item is subjected to the "weights" assessment in the next step, being declared by percentages. These weights are determined empirically and represent the weightiness of the particular item in a given category of assessment. The value of the weight of each item varies in the range from 0 to 100%.

For the purposes of the structure assessment a sheet form was developed, where there were recorded all relevant parameters known from the structure. An example of the form is documented in Table 3.1.1.

In the initial evaluation essential volume values are summarized namely **the storage capacity** expressed in m^3 (Table 3.1.2). This value is the sorting feature, which is based on the value of the original geological reserves of natural gas or crude oil, according to approved reserves calculation. This value can be modified in the event that the actual volume of extracted hydrocarbons exceeded the value of the real achievable exploitability. In such cases, the data referred to in the text of the original hydrocarbons reserves were reviewed on the basis of the calculation of the reserves according to the drop of pressure in the deposit.

The CO_2 storage capacity represents the amount of carbon dioxide that can be potentially stored in the structure.

In the case of qualitative parameters describing the "**Appropriateness**", which assessment can reflect multiple variables, we have chosen a range of **1-5**, in which the lowest value expresses the highest quality (Table 3.1.3). We have assessed the six items - appropriatness criteria, which deal with the description and assessment of the hydraulic properties of the reservoir, the primary and secondary sealing, chemical reactivity of the environment, the existing infrastructure of the deposit and the technical tightness of probes.

In the event that **no data are available** for the assessment, **value 6** is used for such classification. This reflects the value of the maximum risk and the fact that it is necessary to begin to acquire such data for the assessment.

Similarly, we have approached the "**Reliability**" assessment, in which the selection reflects the existing status of geological and deposit situation by means of available technical tools, reference and evaluation of the facts, whether it's a two- or three-dimensional versions of the models and seismic measurements. The range is set to **1-3** and the maximum value represents absence of the selected item (Table 3.1.4).

In the case of logical opinions - category "**Conflicts of Interests**" this range is **0 to 1**, where **1** confirms the

Tab. 3.1.1 Table presenting the parameters for the object assessment

Field	**Reservoir**

General Data

Location	
Structure	Single / Multilayer, comprising reservoirs
Mining Licence	
Exploration Area	

Field Location

Emission Sources Type		Existing	Planned
Emission Volumes [tonnes]		Existing	Planned
Emission Rates [tonnes/day]		Existing	Planned
Pipeline Routes to Sources [DN, PN]		Existing	Planned
Distance to Sources [km]		Existing	Planned

Exploration/Production History

Discovery Date	
Start of Production	
End of Production (anticipated - if operated)	

Primary Reservoir Conditions

Initial Reservoir Pressure [MPa]	
Initial Pressure Gradient [kPa.m^{-1}]	
Reservoir Temperature [°C]	

Reserves & Production as of 01/01/2009 (@ 15 ºC, φ=0)

IGIP, OGIP [10^6 m^3], [10^3 tonnes]		
Cumulative Production [10^6 m^3], [10^3 tonnes]		
Remaining GIP [10^6 m^3], [10^3 tonnes]		

Actual Reservoir Conditions as of 01/01/2009

Reservoir Pressure [MPa]	
Reservoir Temperature [°C]	

Geological & Reservoir Data of Target Horizon

Reservoir Rocks	
Geological Age	
Type of Trap	
Productive Interval Min - Max [m]	
Productive Area [km^2]	
Type of Border	
Net Pay Min - Max [m]	
Porosity Min - Max [%]	
Permeability Min - Max [mD]	
Effective porous volumes available for CCS	

Geological & Reservoir Data of Overburden

Reservoir Rocks	
Net Pay Min - Max [m]	
Productive Area [km^2]	
Integrity of caprock	
Capillary Threshold Pressure Measurements	
Fracturing Pressure Measurements	

Existing Reservoirs above the Caprock (in case of leakage)

Reservoir Rocks	
Interval Min - Max [m]	
Productive Area [km^2]	

Chemical Properties of Gas

Methane [%]		
Inpurities [%]		

Geological & Reservoir Data of Surroundings

Reservoir Rocks	
Interval Min - Max [m]	
Distance to the Target Reservoir [km]	

Chemical Properties of Reservoir Water

pH		
Mineralization [kg.m^{-3}]		

Chemical Properties of Crude Oil

Gravity [g.cm^{-3}, °API]		
Special Components		

Well Inventory

	Number
Drilled Wells in Total	
Existing Wells	
Safe P & A Wells	
Wells to be Additionaly Tightened	
Wells Available for CCS	
Wells to be Reopened for CCS	

CCS Operation

CO$_2$ storage volume [m^3]		
CO$_2$ injectivity per well [m^3]		
CO$_2$ - injectivity per reservoir [m^3]		
Wells Required for CCS		
Maximal Pressure Gradient [kPa.m^{-1}]		

existence of a conflict of interests, which either complicates or temporarily restricts the use of the site/deposit/ part of a deposit for CCS projects (this proposal is supported by the idea that, in the case of a decision on logical opinion the "absence" of competing projects represents the favourable assessment = **0**, see Table 3.1.5).

In this process the conflicts of interests are assessed as competitive mining operations, which represent the upcoming projects, works in progress, or other methods of rock structures utilisation than the CO_2 storage, and under these circumstances, they reduce, or fully eliminate the potential possibility of applying such a structure in the CCS project. See the attached Table.

We evaluate the "**Threats**" in the range of **1-3** (see Table 3.1.6) in order to categorize quite strictly the types of threat that may arise from the CO_2 storage. Because storage safety is a priority, the negative ratings in this area are considered to be a serious obstacle to take advantage of the potential of the structures. We assume that the

increasing emphasis on economically sustainable solutions must not lead to a reduction of environmental liability treshhold and we do not consider any interim solution to be adequate the time and means invested in the storage. Therefore, the solution with the least impact on existing or developing infrastructure has a value of **1**, while the worst one has got a value of **3**.

In the event that the item has not been detected in any category, it has assigned value on 1 greater than the highest (within the meaning of the worst) value of the item in the category.

For a summary evaluation of different categories, we have introduced the classification of each category, based on the value of the weighted average of the all items in the category (Table 3.1.7). Subsequently, each weighted average value there was assigned a textual assessment (classification). All the textual assessments (textual classifications) are contained in the Table of classifications.

Tab. 3.1.2 Storage capacity of the object

Chances and Risks (description and evaluation)		1-5	
CO₂ - storage volume			
m³ IGIP (initial gas in place) according to drop in pressure		Volume	Suitability
CO₂ - storage capacity			
kT calculation according to actual extraction		Capacity	

Tab. 3.1.3 Appropriatness of the object

	1-5	
CO₂ - injectivity for the wells/reservoirs		
	100%	
	1-5	
Geological tightness of the reservoirs for long-term conditions		
	100%	
	1-5	
Chemical Reactivity of Reservoir, Caprock and Fluids		
	100%	
	1-5	
Operation wells required for the long-term CO₂ – injection		
	100%	
	1-5	
Technical tightness of wells in the field		
	100%	
	1-5	
Distance of the storage locations to existing/planned power stations		
	100%	

Tab. 3.1.4 Reliability assessment

	1-3	
Seismic survey (missing, 2D, 3D)		
	100%	
	1-3	
Geological Model (missing, 2D, 3D)		
	100%	
	1-3	
3D Dynamic Model (missing, short term,long term simulation)		
	100%	

Tab. 3.1.5 Conflict of interest

0-1

Existing Production of Gas/Oil	100%

0-1

Existing Plans for Production of Gas/Oil	100%

0-1

Existing Plans for Gas Storage	100%

0-1

Depleted and Abandoned Field/Reservoir	100%

Conflict of Interests

Tab. 3.1.6 Assessment of Threats

1-5

Distance to Municipalities	100%

1-3

Existence of Potable Water	100%

1-3

Effects Assessment	100%

1-3

Risk Characterisation (safety and integrity, uncertainties,...)	100%

Threats

Tab. 3.1.7 Summary assessment

Category	Average classification	Classification range	Overall classification
Suitability			
Reliability			
Conflict of interests			
Threats			

Tab. 3.1.8 Table of classifications

	Appropriatness			Reliability			Conflicts of interests			Threats	
	Classification (1-5)	Range of weighted mean		Classification (1-3)	Range of weighted mean		Classification (0-1)	Range of weighted mean		Classification (1-3)	Range of weighted mean
1	Very high	1.000-1.4999	1	High	1.000-1.499	0	Negligible	0.000-0.099			
2	High	1.500-2.499	2	Moderate	1.500-2.499	1	Very low	0.100-0.299	1	Low	1.000 - 1.499
3	Moderate	2.500-3.499	3	Low	2.500-3.500	2	Low	0.300-0.499	2	Moder. relevant	1.500- 2.499
4	Low	3.500-4.499	4	Insufficient	>3.500	3	Relevant	0.500-0.699	3	Very relevant	2.500- 3.500
5	Very low	4.500-5.500				4	Very relevant	0.700-0.899	4	Excessive	<3.500
6	Not applicable	>5.500				5	Threathening	0.900-1.099			
						6	Inconvenient	>1.100			

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The weighted mean (classification) is calculated according to the relationship:

$$Klas = \sum_{i}^{N} \frac{Vi \times Ki}{\sum_{i}^{N} Vi}, \quad \text{where}$$

Klas - the resulting value of classification category
N - number of items in a category
V_i - the weight of the i-th item category (0-100%)
K_i - the value of the i-th item categories ("mark")

For the purpose of CO_2 storing there have been processed 5 deposits (30 deposit objects) of natural gas and oil in the East-Slovakian Basin and 10 (20 deposit objects) within the Vienna Basin.

In the **East-Slovakian Basin** there was calculated the total amount of CO_2 storage capacity of **7.07 Mt** in 30 deposit objects and in the **Vienna Basin** approximately **12.2 Mt** in 20 deposit objects. The affiliation of deposit objects into a lithostratigraphic sequence in the Vienna Basin is presented in the Figure 3.1.1., the distribution of individual deposits studied is in the Fig. 3.1.2.

Similarly, in the East-Slovakian Basin the affiliation of deposit objects in the lithostratigraphic sequence is presented in the Fig.3.1.3 and the location of the deposits is documented in the Fig. 3.1.4.

The most appropriate object from the perspective of the magnitude of the storage capacity in the East-Slovakian Basin is the deposit **Ptrukša 4. Sarmatian Block IX b** with the storage capacity of 571.7 kt, which has been classified in terms of the magnitude of storage capacity among the inconvenient ones. The suitability and reliability of this object is in the midst of the classification. This implies that the object is from the point of view of capacity suitable only for the pilot project.

From the perspective of the magnitude of the storage capacity in the Vienna Basin is the most appropriate is deposit **Láb, Láb Horizon – the Early Badenian West and the East** with the storage capacity of up to 2,475.7 kt which has been classified in terms of the magnitude of the storage capacity among the small ones. The suitability and reliability of this object is low, the capacity is not sufficient for industrial range of storage.

As we can see from the above capacities, despite the fact that all the proposed objects (including regional aquifers) are the most thoroughly characterised by relevant and verifiable data, in terms of industrial scale they are barely sufficient. In the summary assessment we reach the cummulative storage volume exceeding million tonnes only from both basins (average injection annual capacity ranging from 500-2,000 kT). This would mean that the objects could serve only for pilot (100 kt <) or demonstration (> 100 kT) phases. Another disadvantage is the fact that the horizons worth of interest have been often split into several partial horizons, what would brought complications of a technico-economic nature for the potential CO_2 injecting. We do not want to diminish the importance of those rated deposits, because both of these stages represent a fundamental step towards storage of industrial scale, which can be applied to other objects, suitable for the CO_2 storage. We point out that in the calculation the volume of the underlying local aquifers has not been accounted for.

The largest volume of the original geological reserves has been found in the deposit Zwerndorf-Vysoká and its deposit object the **Main Horizon at the base of Middle Badenian** and its immediate superincumbent - the **"E Horizon" of Late Badenia**n. Despite the above fact (the original reserves may reach approximately 28 billion m^3), these objects have not been included in the submitted list, because the processing of any application for their use must be preceded by an interstate agreement, which would be elaborated within the meaning of the law modifying the regime.

Despite the fact that this deposit has not been assessed according to the above criteria, we have to emphasize some of its parameters, suitable for the objectives of the task. Althogh the current situation is not convenient, in a term of 10 to 20 years a view for this object can vastly change, and it can find its use in many ways, depending on the developments in the energy field. Theoretically, it can be expected the unification of the two countries views to its further use. For this reason, we have tried to summarize all available data on its possible use and design. Due to the size and importance of the structure we have evaluated this deposit in the following section separately.

3.2 Vysoká Zwerndorf

This deposit is processed separately, because it is a unique structure, with very high theoretical potential for the benefit of CO_2 storing.

The deposit is located in the southern part of the Záhorská nížina Lowland, in the cadastral territory of municipalities Vysoká and Láb. The deposit is the largest accumulation of hydrocarbons found in the former Czechoslovakia. The main gas-bearing object - basal Middle Badenian horizon and its superincumbent Late Badenian designated as the "E Horizon" are developed both in the Slovak and Austrian territory. The bulk of the deposit is developed in the Republic of Austria, which bears the name Zwerndorf – the ratio between the Slovak and Austrian sections is approximately 1:2. According to unverified data of April 1, 1960, in the Austrian part of the deposit there were calculated 16 billion m^3 of gas. It was evident that the uncontrolled mining shall influence the use of reserves in the two states. For this reason, since April 1, 1960 the agreement has been in force between the Government of Czechoslovakia and the Republic of Austria on the extraction of common oil and gas deposits. At the Slovak territory the deposit was verified by an irregular network of boreholes with spacings of about 500 m, reaching depths in the range of 1,030 m (borehole V-7) to 3,085 m (borehole V-4) - see Fig 3.2.1.

Geological situation and past deposit- mining data

The deposit is a southern continuation of the Láb-Lakšárska Nová Ves stripe, whose peak antiform is located in the Austrian territory in the area of Zwerndorf-Baumgarten. From the northern Láb deposit structure it is separated by a transverse depression.

VIENNA BASIN
LITHOSTRATIGRAPHIC SCHEME

MILLION YEARS	EPOCHS	STAGES	VIENNA BASIN (Northern part) LITHOLOGY	FORMATION & MEMBERS	RESERVOIRS & FIELDS
5.3	PLIOCENE			BRODSKÉ FM.	
7.1	MIOCENE / LATE	PONTIAN			
		PANNONIAN		GBELY FM.	
				ČÁRY FM.	
				ZÁHORIE FM.	
11.5				Kyjov Mb.	8th Suchohrad - Gajary (UGS conv.)
13.6	MIOCENE / MIDDLE	SARMATIAN		HOLÍČ FM. Karlova Ves Mb.	
14.6		BADENIAN		STUDIENKA FM. Sandberg Mb.	1.,3., 4. Gbely B-Oil Field 6. Gbely G - 105 Oil Field Late Badenian Gajary - 146 Gas Field, Suchohrad - 62 Gas Field, Jakubov - 63 Gas Field
16.5				JAKUBOV FM. D.N.V. Mb. LANŽHOT FM. Zohor Mb.	1b Gajary-Báden Oil and Gas Fields 2 Dúbrava Oil Field. Jakubov West Oil Field
17.5	EARLY	KARPAT		ZÁVOD FM. Jablonica Mb. Šaštín Mb. LAKŠ.N.V. FM. Týnec Mb.	
19.1		OTTNANGIAN		LUŽICE FM. upper part PLANINKA FM. Štefanov Mb.	Ottnangian Cunín Oil Field*
22.5		EGGENBURGIAN		LUŽICE FM. lower part Brezová Mb. Chopov Mb.	
23.4		EGER.			

* Oil Production also from the top of the Flysch Nappes below the Neogene Base

shales   sandy shale ("schlier")   sands   conglomerates   limestones   coal layers

Fig. 3.1.1 The affiliation of hydrocarbon deposits in the lithostratigraphic sequence in the Vienna Basin
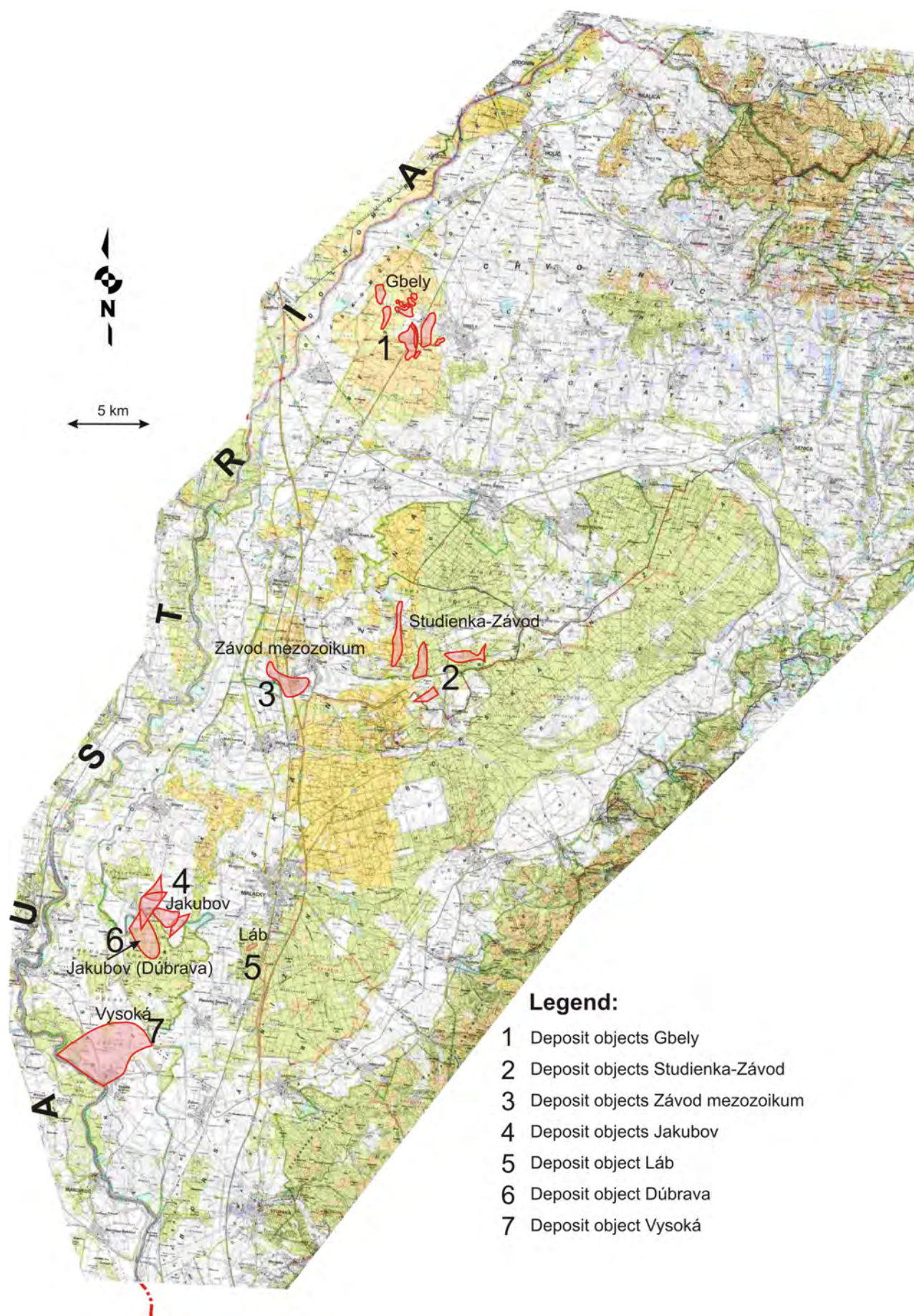
Fig. 3.1.2 The assessed hydrocarbon deposits in the Vienna Basin

EASTERN SLOVAKIA BASIN
LITHOSTRATIGRAPHIC SCHEME

MILLION YEARS	EPOCHS	STAGES	EAST SLOVAKIAN BASIN LITHOLOGY	FORMATION & MEMBERS	RESERVOIRS & FIELDS	
	PLIOCENE			ČEČEHOV FM.		
5.3						
		PONTIAN		SENNÉ FM.		
7.1						
	LATE	PANNONIAN		SEČOVCE FM.		
11.5				PTRUKŠA FM.		
		SARMATIAN		STRETAVA FM.	4th	Ptrukša Gas Field
					2, 3rd	Stretava Gas Field
					8th	Senné Gas Field
13.6	MIOCENE MIDDLE			KLČOVO FM. LASTOMÍR FM.	9, 12th	Bánovce Gas Field
14.6		BADENIAN			16th	Trhovište Gas Field
				ZBUDZA FM. VRANOV FM. MIRKOVCE FM. HRABOVEC FM.		
16.5				KLADZANY FM.		
		KARPAT		SOĽNÁ BAŇA FM. TERIAKOVCE FM.		
17.5						
19.1	EARLY	OTTNANGIAN				
		EGGENBURGIAN		Čelovce Mb.		
				PREŠOV FM.		
22.5						
23.4		EGER.		BIELY POTOK FM. (SOLIVAR FM.)		

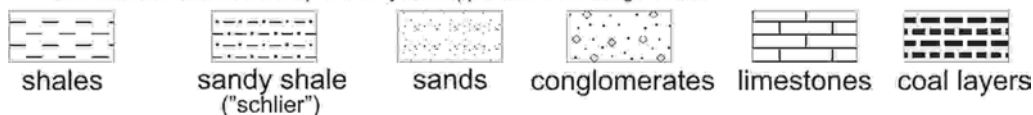| shales	sandy shale	sands	conglomerates	salt	coal layers	tuffs and tuffites	volcanic bodies

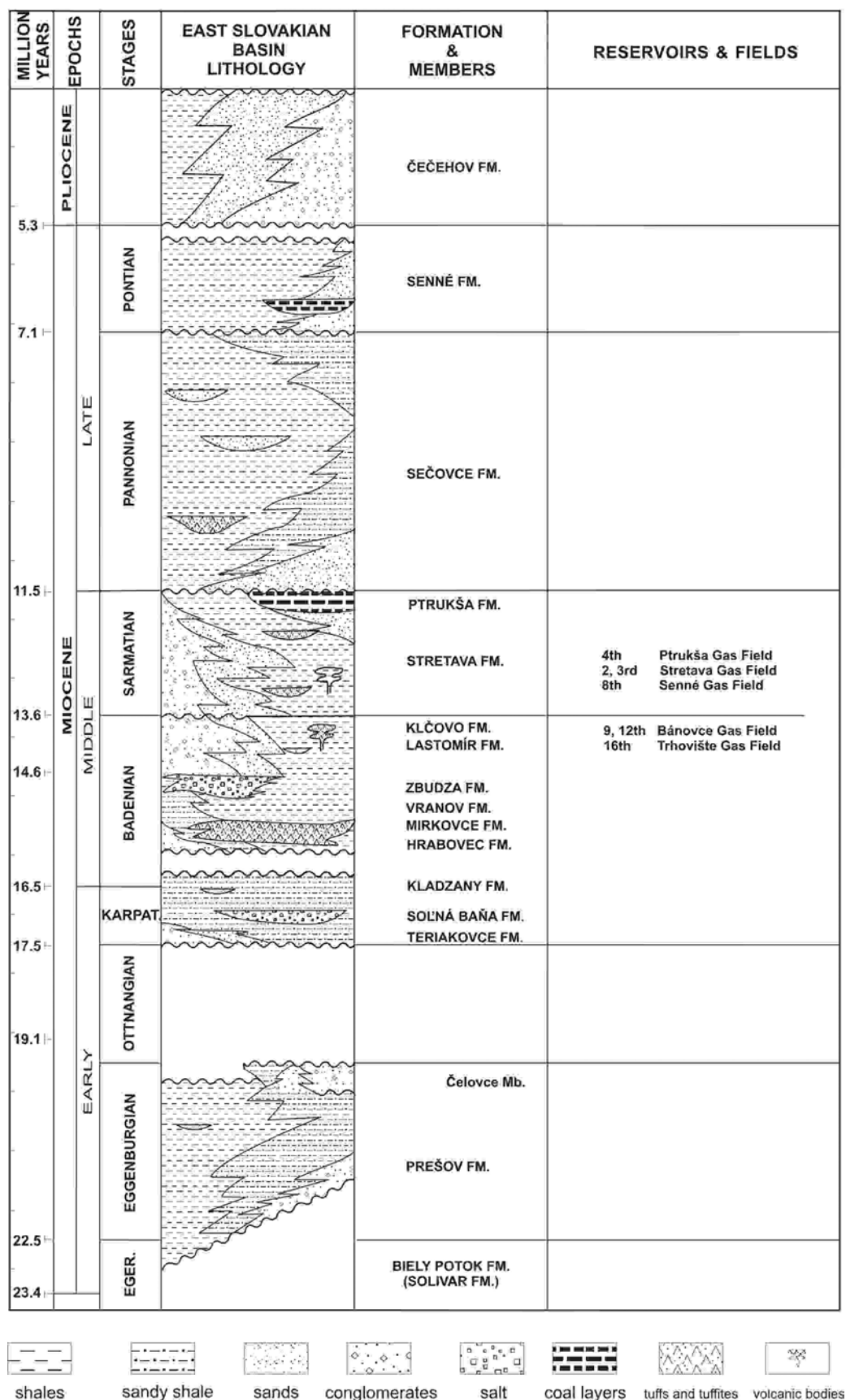Fig. 3.1.3 The affiliation of hydrocarbon deposits in the lithostratigraphic sequence in the East-Slovakian Basin
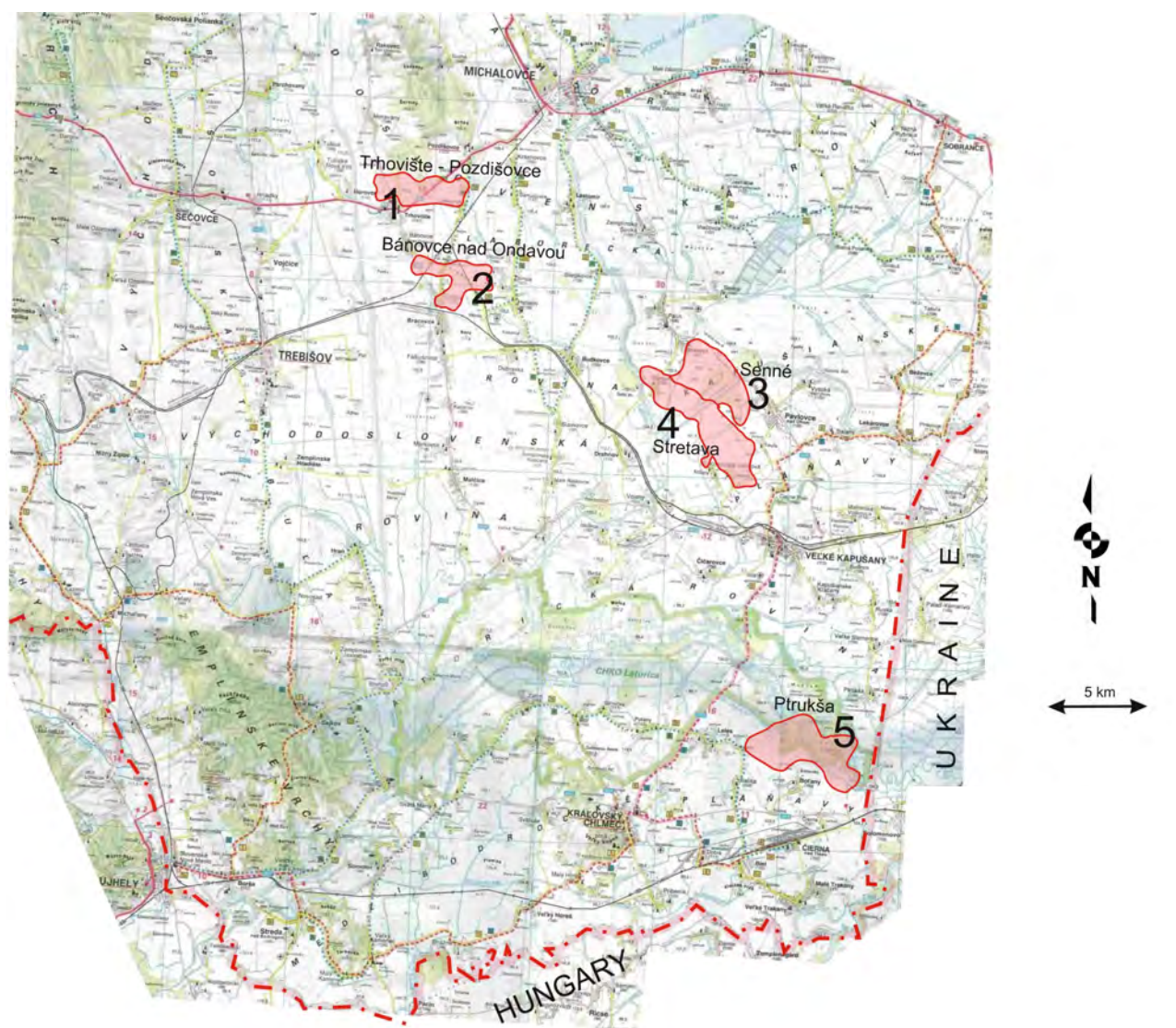
Fig. 3.1.4 Assessed hydrocarbon deposits in the East-Slovakian Basin

According to the result of the borehole Vysoká 4, in the Neogene basement the Hronicum dolomites are present what is the proof that the deposit elevation belongs to the longitudinal Láb- Lakšárska Nová Ves stripe of the NE direction. The Hronicum carbonates basement was met at a depth of 2,800 m.

The deposit is located at the stratigraphic range between Badenian – Pannonian and consists of twelve partial horizons. Mainly sandy strata are present with an average thickness of 5-10 m, some of them are lithologically divided into several hydrodynamic units. The exception is the main gas-bearing object – the base the Middle Badenian with a thickness of deltaic sedimentation products around 500 m. Its gas-saturated part reaches a thickness of nearly 60 m. The reservoir (collector) rock is cemented by fine-grained calcareous-clayey sand with intercalations of calcareous clays (Fig. 3.2.1).

In the course of mining an expansion regime prevailed with more or less limited influence of the water component activity (Hlavatý, 1994). This finding is at odds with the data from the Austrian side, where, by contrast, the aquifer was active, participating significantly in the deposit regime (Lorenc, 1968). By contrast, in the main Late Badenian horizon (E horizon) due to large cubage of the underlying water its activity was significant. Nevertheless, the rational management of mining achieved coefficient of exploitability against the planned one 0.7 up to 0.77. More than 97% of gas content was CH_4. The Badenian waters belong to alkali-haline, calcium-chloride type. Of the same character are also upperlying Sarmatian waters.

The calculation of the reserves from the 1960s (unauthorized) featured for basal Late Badenian horizon the reserves in the amount of 10 billion m^3 (not approved by

Fig. 3.2.1 Vysoká, horizontal extension of "g"sand of Middle Badenian (base)

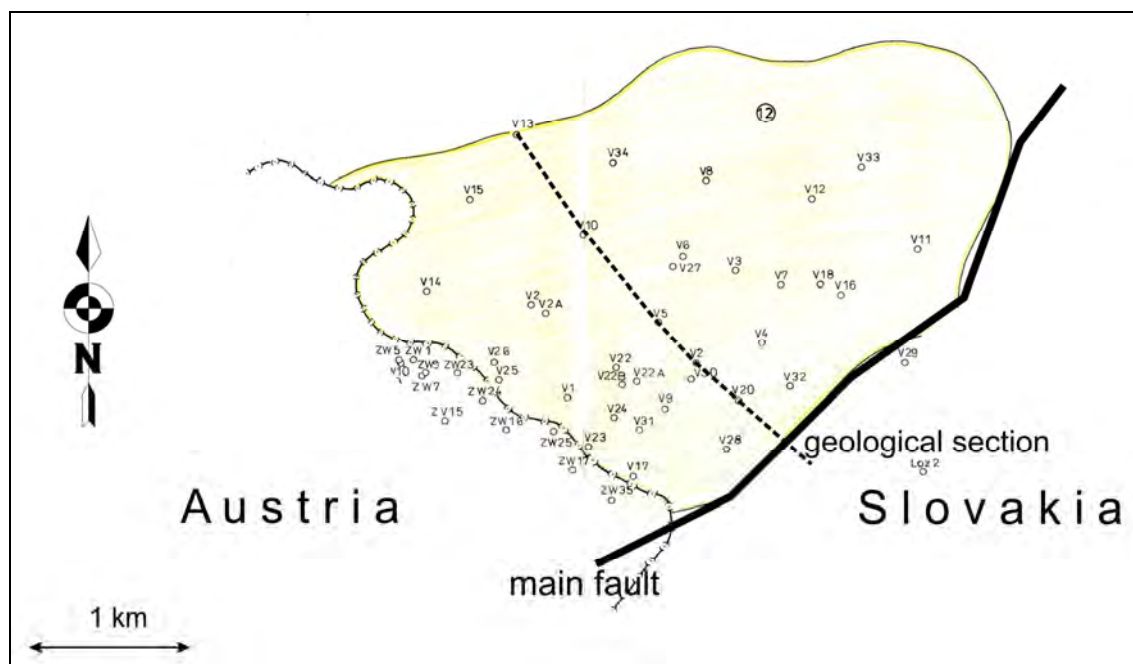CRC – Commission for Reserves Classification). Later on, the conversion of reserves in terms of the Decree No. 6/1992 Coll., was implemented, with the status of January 1, 1994 (Hlavatý, 1994). The reserves, which were originally presented in categories A, C1 and C2 have been downgraded to category Z-1, on the grounds that they were verified and depleted reserves and the geological setting of the deposit and its shape had already been solved. The deposit is currently depleted and water-saturated, from the Slovak balance of reserves remains 36 821 000 m^3 (36.8 million cubic meters) of gas in the main horizon of Middle Badenian. This gas is located in the highest positions of the deposit in the area of Zwerndorf Baumgarten on the Austrian territory and in the case of reservoir building it will find its use as "cushion gas". The amount of depleted reserves within the Slovak section is 3 billion m^3.

The main part of the deposit – basal horizon of Middle Badenian is a broad brachyanticline, of the southwest– northeast direction, which is almost not tectonically disrupted (Figure 3.2.2). The exception is the tectonic boundary to the southeast. This is a Láb fault system where a vertical throw in Sarmatian is 150-200 m with a slope of $45°$ to the southeast. There is also a tectonic restriction in the area of the state boundaries (drillings Vysoká 17, 23 and Zwerndorf 23), the vertical throw, however, is greater than the effective thickness of the gas-saturated layer. The elevation peak was detected by the boreholes Vysoká 1, 4, 20, 21, 22 and 25. Towards the East and the North the elevation is declining at an angle of $2°$. The average depth of the contact gas/water was determined at 1,348.1 m. Since the launch of mining there has been observed a drop in the deposit pressure in the main part of the deposit. Accounting for this it has been deduced on the existence of gas (expansion) regime. According to Hlavatý (1994) the deposit consists cur-

rently of 12 blocks with non-balance reserves in the category of Z-1 - in total 3 008 billion m^3, of which the main horizon No. 12, of Middle Badenian base stores 2874681 million m^3 of gas, which represents virtually 95% of the entire deposit. (To this number there must be added the 37 million m^3 of balance reserves in the category Z-1 for the cushion gas in the block No. 12, which, in the case of the transformation into storage space, would be replaced by carbon dioxide). The annual consumption of gas in Slovakia is at the level of almost 6 billion m^3. This brings us to the conclusion that in the case of the transformation of the deposit into the CO_2 storage, we would be "theoretically" able to get the volume of gas through gradual CO_2 storage in the Main Middle Badenian horizon covering nearly 50% of the annual gas consumption of Slovakia.

The uppermost horizons 6th Pannonian and 8th Pannonian or 2nd and 4th Sarmatian are shallow-lying for the purposes of the carbon dioxide storage and therefore excluded from consideration due the impossibility of achieving its supercritical status.

The mean value of permeability in the deposit (the average from the laboratory measurements and sounding) was established at 108 mD. The value of the absolute permeability in such amount corresponds to the saturation of the residual water at the rate of 25%. The gas saturation coefficient can then be considered to be 75%, while maintaining the same deposit pressure. The porosity is set to a value of 26%.

The deposit pressures were calculated on the basis of static pressure measured at the mouths of boreholes. At the average depth of the basal horizon Middle Badenian of 1 455 m the average pressure was calculated at 12.3 MPa.

The deposit temperature was determined in accordance with the Austrian side to 64 °C.
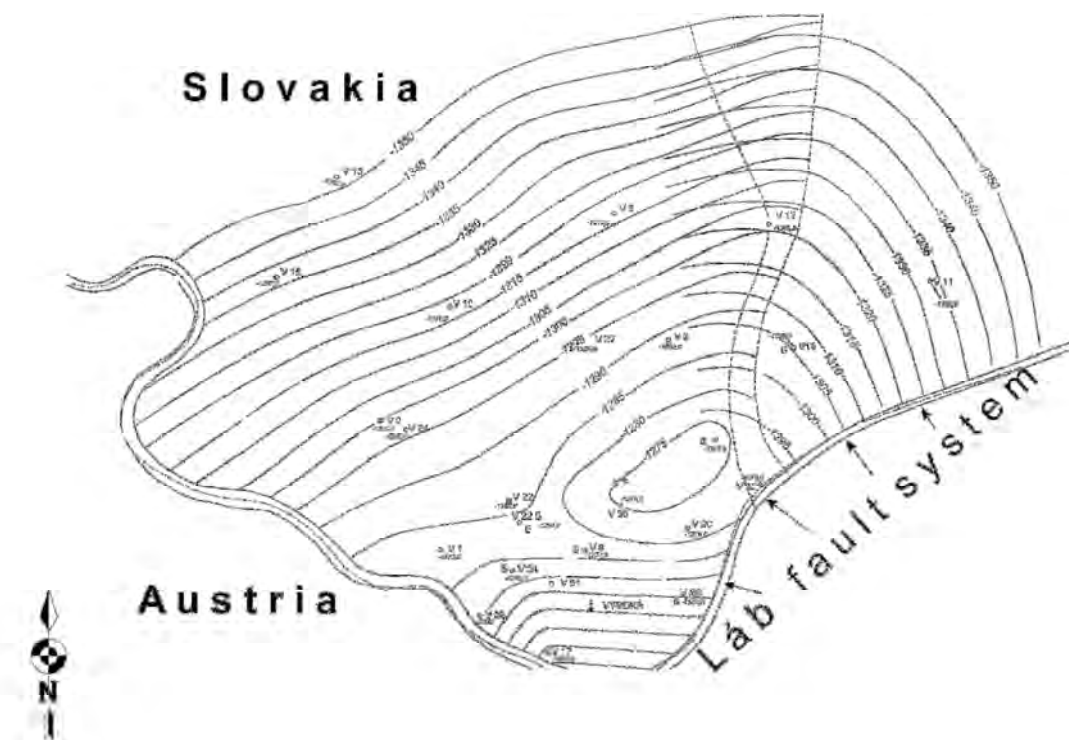
Fig. 3.2.2 Dephts of the main productive horizon

The issue of CO₂ storing in the deposit

From the above it is evident that the deposit (under this term we mean the main deposit horizon - Middle Badenian base) fully meets the P and T criteria, in order to achieve the supercritical state (7.2 MPa, 31.1 °C) that are required for a structure suitable for the CO_2 storage. The safety in terms of the risk of leaks, according to the geological survey, is at the appropriate level, as well. (There were no leaks for a few million years until the deposit discovery).

In theory, in the cases of such hydrocarbon deposits, the premise is accepted that all extracted pore spaces containing gas and emptied due to mining will be replaced by carbon dioxide. This assumption is generally valid, if the reservoir is not in contact with the aquifers, or it is not flooded with water during the secondary or tertiary gas recovery. Another assumption is that the integrity of the roof sealing will be preserved, therefore the pressure of the CO_2 injected will not exceed the original deposit pressure. This estimate is conservative, because the pressure can exceed the capacity of the original pressure in such a long time on a temporary basis, which ensure that it does not exceed the limit of tensile cracks generation, or reactivation of existing faults (according to Bachu and Shaw, 2005). In this case, the storage capacity increases as a result of CO_2 compression and the possibility of obtaining more pores space. *Effective storage capacity* depends upon the *internal* reservoir characteristics, taking into account the the water invasion, extrusion, gravitation force, heterogeneity of a collector and the effects of water-saturation. *Practical storage capacity* is dependent on *external factors*, such as technological limitations, storage security, distance of the CO_2 producers, infrastruc-

ture, economic regime given by the legislation ... (Bachu and Shaw, 2005). From this point of view, we have to perceive the following "estimates" as indicative, because the number of factors is not possible to anticipate although modeling of a particular activity on the basis of reservoir engineering should be an integral part of the work. In any case, the calculated CO_2 storage capacity in this deposit can be regarded as the *effective storage capacity*.

The issue of aquifer in this case is one of the decisive factors. According to the data from the mining (Hlavatý, 1994) the aquifer influence in the main gas-bearing horizon at the base of Middle Badenian was not significant. However, the deposit has been flooded now (since 1972), so it will be necessary to count at any experiments with the opposite aspect. In such cases, for the ousting of all water and the achievement of the original aquifer reservoir volume, the CO_2 pressure will be significantly above the initial deposit pressure, what constitutes a risk factor. According to the above authors on the basis of statistics based on a study of thousands of gas horizons from the province of Alberta in Canada, in the case of "strong aquifers" – the ratio of the volume of water/gas ≥ 10 is responsible for the reduction in the calculated capacity by an average of 30% in a deposit (range 0-48%). In the case of "weak aquifers" the ratio of water/gas < 10, the storage capacity reduction is virtually negligible; on average, about 3% (according to Bachu et al., 2004).

Among favourable factors we can certainly include the petrographic characteristics of the collector horizon. Its share of the calcareous component may in the case of storage activities in the optimal injection mode positively affect the increases of the effective storage capacity,

especially in the longer term – application of the mineral sequestration and trapping, thus reducing the CO_2 pressure in the elevation part of the structure.

In the introduction of this chapter we have stated that 36.8 million m^3 of methane remains as a Slovak proportion at the Austrian side, which would in the case of the transformation of the deposit into the gas reservoir serve as cushion gas. It offers the opportunity to extract this gas here and its replacement by CO_2, which would act as a cushion, even if the deposit served as a reservoir of methane. The reservoir simulation of such methodology suggests that when using CO_2 as a cushion gas it is possible to increase the capacity of the methane up to 30%! (Oldenburg, 2003), provide the storage reservoir is in supercritical depths – as consequence of density changes. A critical element is a so-called mix zone between the methane and CO_2. Higher density and viscosity of carbon dioxide to methane should minimize this problem (Oldenburg, et al., 2001). Similar considerations appeared already in the territory of Slovakia, when was deliberated using of natural CO_2 gas deposits Sereď as cushion gas for deposits Veľké Kostoľany and Ivánka pri Nitre in the Podunajská nížina Lowland (Hrúziková, et al., 2006).

If we add to these considerations the capacity issue, so according to the above authors we have in the Slovak part a space from which it was extracted 3 billion m^3 of gas, and where it remains the same amount, that is 3 billion cubic meters of gas still not extracted in the underground (just to illustrate in the year 2010 in the District Mining Authority Bratislava area 65.746 million m^3 gas were extracted). The total volume of 6 billion m^3 of gas (volume at the surface) transformed through the density and the formation factor corresponds to the imposition of 11.7 million tonnes of CO_2. In doing so, we are still remaining in the area, which was, or is occupied by the gas. Logically, the original deposit space must be increased on the volume of the water aquifer, because the maximum thickness of the reservoir horizon is 500 m, the gas-bearing has or had been about 60 m prior to the start of the mining operation. It is obvious that the maximum values cannot be accounted for; it is possible to calculate the exact volume of aquifer according to drillings – but to the resulting storage capacity, which is not theoretical, but in the sense of the pyramid effective. We can add almost the same amount of storage in the aquifer that is several times thicker than the gas-bearing zone. In this approach, it is fair to count with a capacity of 25 million tonnes of CO_2, which satisfies the attributes of the repository of industrial character.

It should be stressed that even the water of the aquifer is interesting on the basis of analyses of pumping tests conducted by ČND Hodonín. The following considerations can be deduced from them:

The chemical composition of the water is quite monotonous, the water corresponds to the natrium-chloride type. S1 component (Cl) in the Badenian collectors environment ranges in the interval of 94.0-95.0 mval %. The second most abundant component is Na-HCO$_3$ (natrium-hydrogen-carbonate), which takes the value of 3.2-4.6 mval %, indicating the minimum impact of infiltration

degradation in the geological past, as well as the presence from the hydrogeochemical point of view. This factor is also a very important *positive* contribution to the security characteristics of the repository from the perspective of potential losses, suggesting that the structure is likely to be well sealed.

From the genesis point of view the water is of marine origin, in other words, the original marine waters of the Badenian transgression, which were metamorphosed to a minimum in the water-rock system. This is indicated also by the value of total mineralization, which is moving in the range of 25-35 g.l^{-1} and essentially correspondd to the Badenian palaeosalinity. The hydrogeochemical closeness of the structure testify the values of the coefficient of HCO_3/Cl, ranging from 0.008 to 0.018. The waters show significantly increased content of iodine and bromine, so they can be considered as iodine – bromine waters with healing effects on the human body. At present, in Slovakia natural healing water of this kind are very rare, it is exploited only in Číž Spa (source of Hygiea has a very small yield) and there are plans to use waters of similar composition in Oravská Polhora.

The content of iodine in groundwater in the structure Vysoká has a values range of 10-26 of mg.l^{-1} (both in the main deposit, as well as the overlying Sarmatian horizons) which far exceeds the minimum concentration of 1 mg.l^{-1} iodine ion, required by Decree No. 100/2006. For balneological use of these water bodies it is also very convenient, that they can be applied to the drinking treatments, because they do not contain substances of so-called petroleum origin, which give the water unpleasant sensory properties. An open question remains quantities of water and yield of wells in this structure, since information is missing. From this point of view, it would be necessary to carry out the calculation of these quantities and to determine iodine and bromine contents, because in addition to the balneological purposes they could serve as raw material in the pharmaceutical industry and for the protection of the environment, as a catalyst and a disinfectant (Io). The yield should be determined by the intensity of CO_2 injection. It follows that potentially it could be assessed besides the economic considerations of reserves calculation also with the value added of this requested raw material.

Another positive is the fact that this could be the repository with the EGR application (Enhanced Gas Recovery), thus a higher contribution to the energy base of Slovakia and an undeniable economic benefit for the company, which would implement this activity. Assuming the imposition of around 1 million t/year of CO_2, in the calculated capacity assumes a minimum lifetime of storage of about 25 years. Currently the world's largest volume is being stored in the deposit Weiburn, Canada – about 2.5 million t/a, which is associated with EOR - Enhanced Oil Recovery. In other cases, an average of 0.7-1 million tonnes of CO_2 is stored.

However, it should be noted that this activity requires negotiating with the Austrian partner. To illustrate, that only reserves in the Austrian part of the deposit (16 bil-

Fig. 3.2.3 Vysoká, extent of Sarmatian 7
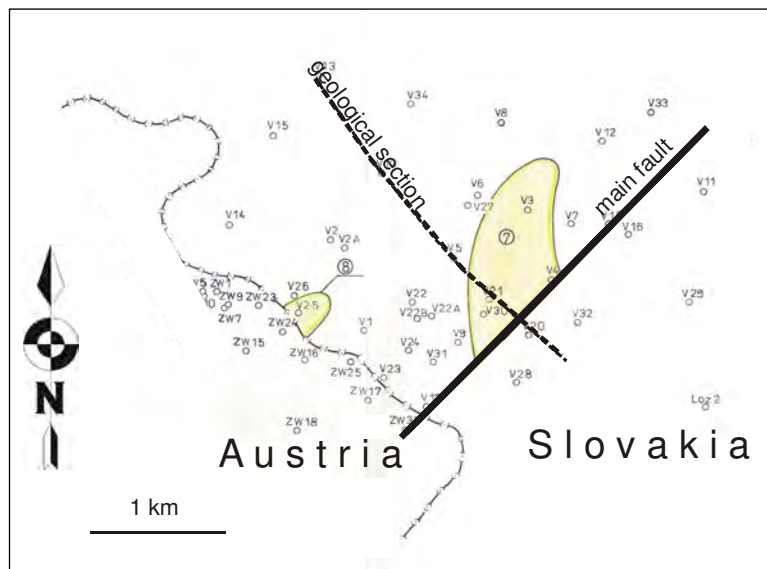
The above parameters ensure supercritical status of CO_2 requested for appropriate storage.

Estimated productive area is 635,000 m^2, cubature 2,413,000 m^3. On the basis of reclassification in the block are calculated non-balance reserves in the category Z1 attaining the volume of 6,030,000 m^3 of gas (Hlavatý, 1994) that represents a "coarse value" of approximately 1.8 million €. If we apply the volumetric principle of calculating the capacity of CO_2 storage, which is the coefficient of volume, gas density and formation factor, so we get the storage capacity in the range of 3,000 to 30,000 t of CO_2. Such amount would be sufficient for the pilot project, moreover, useful information could be obtained for Enhanced Gas Recovery. According to the formula for the aquifers we got negligibly higher value – almost 34 000 tons. It is necessary to consider the effect of aquifer on the above numbers. Gas reserves totaled in the 7th Sarmatian term horizon are not great, but for a small recipient in the vicinity of kind of interest, since the gas contains more than 97% methane. In such a case it would mean the EGR (Enhanced Gas Recovery), so it is realistic to expect a higher yield than calculated reserves. This would be in addition to the undeniably necessary knowledge about the study site, relevant for decision-making criteria (state, the company concerned) in the context of the "political development" in the field of combating the adverse effects of climate change, as well as achieving a certain "economic benefit" in the form of a reduction in the cost of the project.

A very valuable factor from the geological and economic point of view is the fact that the deposit offers unique opportunity to test the pilot stage of carbon dioxide injection into the depths very favourable from both of the above considerations. In the case of a positive result of the pilot stage, it would be possible without moving the infrastructure, only through its extension, to continue in the same place by developing activities to industrial scale, provided an agreement with the Austrian party will be settled. On the Austrian side in the vicinity are also big producers of CO_2 – ŐMV Vienna, industrial companies and Vienna Heating, on the Slovak side Slovnaft, Bratislava, Paroplynový cyklus Bratislava, Calmit Rohožník (Figure 3.2.5).

In addition, here plays a very important role the safety factor of the potential repository. The Láb fault system, or one of its faults, that in the present situation seems to be in theory as a risk factor of potential losses, is common to both Sarmatian and the Badenian horizons, so it is possible in the pilot stage to test, in particular, potential vulnerabilities, valid for the industrial plan, which is very valuable. Both reservoir horizons are amputated by the fault; continuation of the gas-bearing positions towards the Southeast was not detected (Figure 3.2.4). Sponta-

lion m^3) is this space suitable for the storage of approximately 30 million tonnes of CO_2 (not accounting for thevolumes in aquifer). Through simple sum up, we get to the efficient capacities of the entire deposit (Austrian and Slovak parts) excessing 50 million tonnes – and this does not need further comment.

Alternative interim proposal for a pilot project

The issue of additional extraction of hydrocarbon deposits utilizing pressurized carbon dioxide emerged due to purely economic reasons in the 50ties in USA, where the greenhouse gas issue was discussed limited to scientific milieu. This issue was also solved in that time ČSSR, when it was suggested to utilise CO_2 from its natural deposit Sereď in order to carry out additional extraction of the deposits in the Vienna Basin (Juránek, et al. 1968).

According to the survey work only the main gas horizon – base of the Late Badenian (Higher Upper Badenian) and "e horizon" extend to the territory of the Republic of Austria. For the purposes of the pilot project could suit block No 7, marked as 7th Sarmatian horizon that is detected only in the territory of Slovakia (isolated lens) by boreholes V-3, 4, 31 and 30. Boreholes V-5, 7, 9 reached the horizon, but they were negative due to the transition into marls. As this horizon does not extend to the territory of the neighboring state, in theory it could serve for the purpose. Although the horizon is quite inhomogeneous from the viewpoint of the facies, nevertheless such a horizon could be representative of the typical "Western Carpathian" collector horizon (Figure 3.2.3).

The gas-bearing interval is at depths 831 – 869 m below the surface, the effective thickness of the collector layer is 3.8 m. Porosity coefficient should be around 20% (on the basis of data from the 6th Láb horizon), the average pressure is 8.4 MPa, temperature is not stated, but according to an extrapolation from the Main horizon, as well as according to the Atlas of geothermal energy (Franko, et al., 1995), at a depth of 1,000 m below the surface temperature should be over 45 °C.
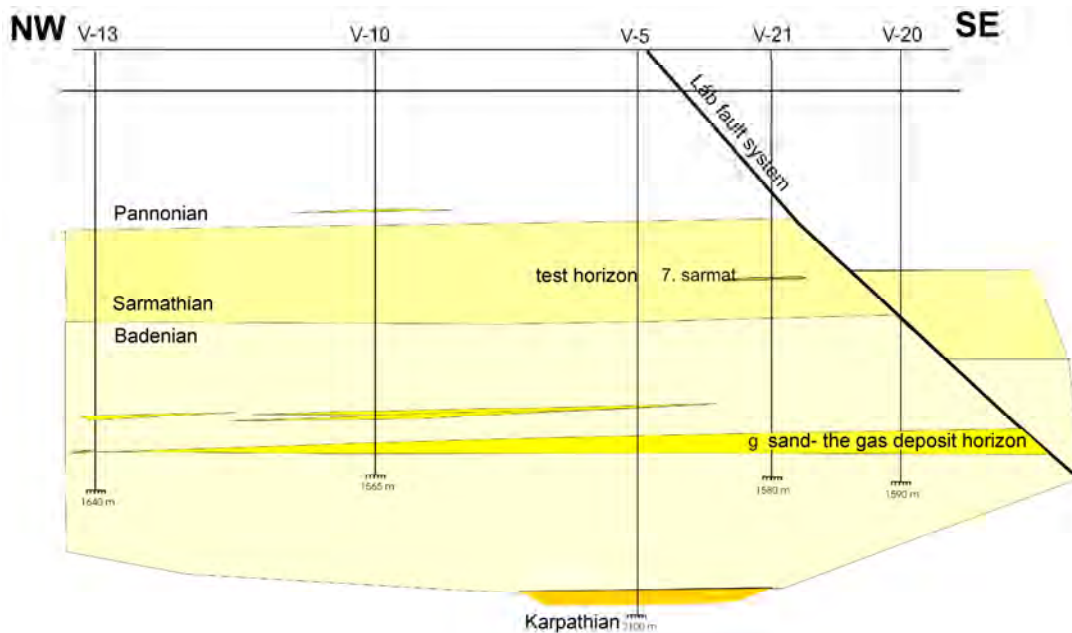
Fig. 3.2.4 Vysoká, geological cross-section through productive horizons

Fig. 3.2.5 The situation of the large deposit Vysoká- gas reserves volume and complexity in terms of share between two states the deposit Vysoká-Zwerndorf, despite the gradual retreat of mining offers numerous alternatives for its economic and ecological use in the next few years.

neous leaks of natural gas that is enclosed in natural trap were not confirmed for few million years ago. Therefore, by substantiated pressurising of collector horizons (the injection pressures shall not exceed significantly the original deposit pressures) it is possible to ensure the hermetic sealing of the reservoir space. In support of this conclusion is that the nature of the faults concluding the structural trap in Middle Badenian has usually good sealing factor, as it is for example, at the deposits in the Podunajská nížina Lowland - Sereď (Majcichov fault) and Cífer (Cífer fault), Cífer (Gaža, 1994, 1994a).

Summary

It is natural and understandable, that any intent, especially one that is oriented into new, non-routine methodologies has its strengths and weaknesses. In the present stage of knowledge, we can present the following:

Problems:

Agreement with ÖMV; the Austrian party would have to agree with the above activities – the need for a study of the Treaty, in particular in terms of cooperation and a time limitation. The Treaty applies only to the Main Middle Badenian horizon and "E" horizon. The above structural blocks are irrelevant regarding methane reserves.

The state of the old boreholes as a purpose built for the injection and monitoring, as well as the potential risk of possible escape routes. It is possible that after 50 years the technical state of the boreholes will not allow to utilise them, on the other hand they can be dangerous as a potential escape route from the CO_2 repository.

The attitude of the public in the case of consideration of the industrial CO_2 repository. Reservoirs of methane are not such a thorn in the flesh of non-governmental organisations and the public, because they belong to the normal civilisation "background".

If positive results of the pilot stage and move into the industrial variant will be reached it would have to be carried out a set of diffuse injection wells, in order to achieve the maximum yield of the gas, which would increase the costs of the project.

Low price of permits area about 4 €/t CO_2.

Benefits:

The pilot-stage 7th Sarmatian horizon does not apply to Interstate Treaty – it is present only in Slovakia.

Similarly, the new act on underground CO_2 storage does not apply to the pilot stage.

In the case of the pilot stage – 7th Sarmatian horizon the collector is 830-870 m deep below the surface, which already guarantees supercritical state of gas and at the same time it reduces economic demands on drilling depths (theoretical depth to achieve supercritical state is 800 m). In the first pilot stage one injection and two monitoring wells would be sufficient.

In the case of the implementation of the pilot project opens up the possibility of additional extraction of residual reserves in this block, which creates "certain" financial counterweight to the projected cost.

Not a very large depth of the boreholes of the main deposit horizon "**g sand**" (up to 1,500 m) in the case where it is not possible to use - recover old drillings.

The appropriate petrographic composition of the collector - increased proportion of carbonate components, which represents the application of the residual trapping, dissolution trapping, as well as mineral sequestration, which is suitable for the long term safety of the repository, as the pressure upon uperlying complexes is reduced – CO_2 sinks to the bottom of a reservoir, or it binds to the carbonates.

Favourable chemical composition of aquifer water of natrium-chloride type with high contents of iodides. These are **scarce and sought after** for balneologic use. After the calculation of the reserves it could be considered iodine and bromine exploitation from the aquifer, as exclusive mineral resources.

Due to the fact that the deposit has been **well geologically sealed** in its roof; tectonic faults are found only on the SE limitation (Láb system, which has a sealing effect), the risk of natural leakage from the reservoir is reduced, provided the **original deposit pressure would not be significantly exceeded**.

Close source of CO_2 (large point sources - Slovnaft 2.5 million t/year, Rohožník – Calmit 1 million t/year, Paroplynový cyklus 0.7 million t/year), all within a radius of 20-40 km. This is in addition raised by railway Zohor – Záhorská Ves passing through the territory of the deposit and offers convenient means of transport for the pilot stage (the parameters of the line speed 60km/h, max. train length 290 m – about 20 standard tanks, 1 suite).

Provided the pilot project will be tested successfully, the possibility of a continuous transition to the deeper main deposit horizon (**g sand**), without replacing the kits and the infrastructure to another location, which is **economically beneficial**.

In this case, the application of geological-deposit-technical knowledge in the pilot project, implemented at the same site to the industrial stage, greatly affects the reliability of the solutions from the professional point of view.

In the event of a decision not to proceed after the pilot phase to the industrial phase, lessons learned from this deposit will be applied to other places in the Vienna and the Danube basins, as well as in the Transcarpathian Basin, eventually.

Global trends in gas prices increase, which after the termination of the pilot stage (5-6 years) may be at a much higher level in comparison with the present, which is related to the deposit reserves extraction with conjoint CO_2 storage.

When engaging the Austrian side in addressing a potential increase in storage capacity, as well as to create better opportunities for the financing of the project from trans-national funds.

The **transformation** of the dominant part of the deposit - Middle Badenian base 12th block – **to gas repository UGSF** – the deposit contains methane reserves (3 billion cubic meters) serving as cushion gas. About the same amount had been already extracted. This would be

probably the biggest gas reservoir on our territory. The alternative would be the Late Badenian "E" horizon, where, however, the capacity is many times less (12th block - g sand -represents 95% of the total reserves). However, considerable economically usable capacity of the gas would remain tied up in the deposit. Of course, we are considering only at the theoretical level, since there are already plans for the UGSF in the Danube Basin (Križovany nad Dudváhom and Cífer).

To extract remaining reserves of methane (cushion) in the main deposit and replace it by CO_2, which would serve as cushion instead of methane. In addition, the amount of CO_2 injection would serve as a medium for pushing out the residual reserves, which could lead to higher capitalization of the deposit. There should be made the decision, how much gas we want to extract; this determines the volume of CO_2 injected. In this case, we are moving in the range of: UGSF (methane) with dynamic exchange system according to designed capacity – static CO_2 storage, provided the theoretical amount (3 billion m^3) of all reserves of natural gas extracted, which are classified as the non-balance ones. Practical use of EGR technology (Enhanced Gas Recovery) has not been sufficiently tested, yet.

To use the 7th Sarmatian horizon as the study one on the basis of the development of the deposit as a pilot project (in terms of time due to possible sources of funding to date.) The gas-bearing interval is at depths 831-869 m below the surface, the effective thickness of the collector is 3.8 m. In the course of the carbon dioxide injecting, in addition to the study of the behaviour of the deposit – technical parameters, the residual reserves of

natural gas would be exploited at the same time (approximately 6 million cubic meters), which would shift the pilot project to economically more favourable relations and it would be a positive impulse for a project proposal. This would actually test out the EGS methodology (Enhanced Gas Recovery) for the first time on the territory of Slovakia and clarify behavior of all relevant parameters, ensuring a secure and permanent CO_2 storage.

Provided the *positive results* are obtained, the pilot phase could be transformed without excessive costs and time intensive transfers to another site, into the industrial phase of deepening and increasing the number of injection and monitoring wells, and with a maximum advantage of specific, targeted knowledge gained at this stage. In the case of *rejection* of the implementation of the industrial repository at this site, the lessons learned can be applied to other, mostly Neogene structures (Vienna, Danube and Transcarpathian Basins) selected for this purpose, because the issue of CO_2 storage is one of the main directions of EU policy in the fight against the adverse effects of climate change.

From the above findings the extraction of aquifer waters is realistic, which have significantly increased concentrations of iodine and bromine in the horizons. The waters of this type are in demand in balneology; the chemical elements can be applied in the pharmaceutical, chemical and energy industries. This fact certainly enhances the economic attractiveness of the proposed activities. For this purpose it is necessary to carry out the calculation of the aquifer reserves and the calculation of the amounts of iodine and bromine, respectively.

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4. Local and regional aquifers

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While the local aquifers are known primarily from hydrocarbon deposits and are "relatively geometrically limited" regional aquifers everywhere in the world have the greatest potential for CO_2 storage. Unfortunately, the relevant knowledge about these structures is insufficient in contrast to the local ones. Apart from structural and non-structural hydrocarbon traps these structures are open (localized predominantly in the basins created by the pull-apart tectonic mode) and, in the case of the CO_2 storage they pose potential threats to neighbouring areas. Everything is subject to the knowledge of the geological situation and tectonic characteristic, which is the crucial one, because it decides about imperviousness, and leakage. Again, we have to point out, that we are dealing with aquifers, which contain saline waters. According to the general adopted criteria, the saline water (unsuitable for drinking and other commercial purposes) is the water with higher mineralization than 1,000 ppm.l^{-1}.

The volume of carbon dioxide that can be stored in an aquifer depends on many parameters defined in ordinary cases very poorly. They are, for example (Chadwick, et al., 2008):

- The volume of the pores in a structural or stratigraphic trap;
- Whether a trap will loose a stored gas due to leakage;
- Proportion of accessible CO_2 saturation in a trap;
- Cases, where only a certain percentage of the repository contains several smaller traps, and only certain number of them can be reached by wells;
- Amount of CO_2 which shall dissolve in saline fluids, contained in the pores;
- Amount of CO_2 which shall be trapped in the form of residual capture, while migrating through capillaries;
- Whether a local or regional hermetic sealing of an aquifer will limit a storage capacity due to CO_2 injection;
- Bulk density of CO_2 and any impurity contained within.

For this reason, there is a necessity in a significant amount of information, in addition to the area of a reservoir, thickness and porosity of a collector, which, however, in most cases are not available. Among the local aquifers we have included the hydrocarbon structures of the Danube Basin, in particular. In this respect, for some others from other territories of Slovakia, their character can be set up on the basis of the results of further works. We present an overview of the objects for potential storage CO_2 in the following text.

4.1 The Danube Basin

Within the Danube Basin we focused primarily on the local aquifers of small gas deposits (Fig. 4.1.2.1), located in marginal areas; however, we cannot exclude that, due to its extensive area, it will be possible to find out appropriate structures of these objects. Therefore, we devote a lot of focus to the lithology of the region.

4.1.1 The geological setting of the Danube Basin

The Danube Basin belongs to the intramountain depressions and extends finger-like between the Core mountain ranges of the Western Carpathians, which define individual partial depressions (Fig. 4.1.1.1).

The Core Mountain ranges of the Malé Karpaty, Považský Inovec and Tribeč are made up of mostly granitoid rocks and Mesozoic carbonatic sediments. Sedimentary fill of the Danube Basin is made up of pelitic, sandy and coarse-clastic rocks of Miocene and Pliocene age (Fig. 4.1.1.2). The area of Central Slovakia Neovolcanites is built of volcanic and volcanoclastic rocks representing the south-western parts of the Štiavnica Stratovolcano and Pohronský Inovec.

In the geological setting of the Pre-Tertiary basement a dominant part take the Veporicum rocks and their envelope, with more or less preserved outliers of Palaeozoic to Mesozoic age. In the South-Eastern part of the territory, behind the Hurbanovo fault, the Pelsö rock units are present, reaching on our territory from Hungary. With the exception of the above mentioned Core Mountains and isolated islands in the NW part of the Levice-Turová Horst near Levice, the Pre-Tertiary subsoil does not crop out within the territory of interest.

The Neogene sediments of the Danube Basin overlie transgressively and discordantly the Pre-Tertiary basement. On the interface between the Neogene sedimentary fill and the basement rocks there have been preserved a few isolated stratovolcanic centres, Early Badenian in
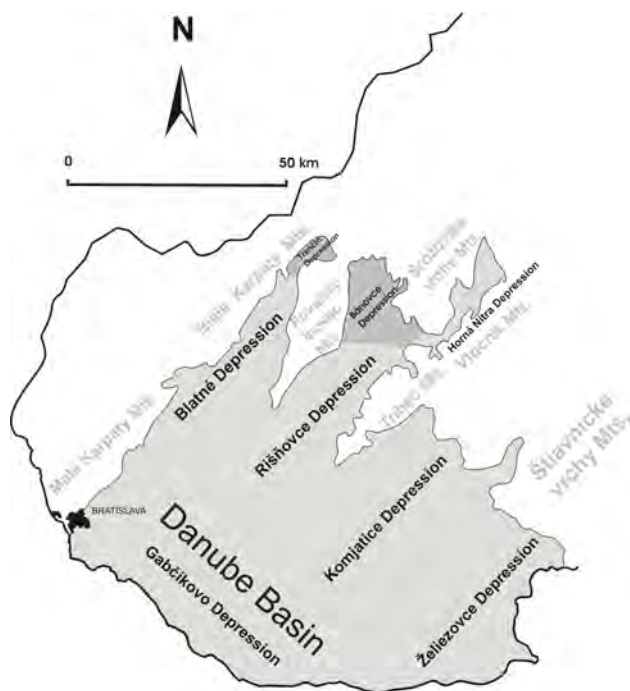
Fig. 4.1.1.1 Regional geological division of the territory of the Danube Basin (according to Vass et al., 1988 compiled by Nagy 2011).

age, representing the buried Šurany volcanites. Into the sedimentary fill in the southern part of the map the volcanoclastic rocks of the Börzsöny Stratovolcano, Early Badenian in age, are exposed; in the northern and eastern part of the territory the Sarmatian, Pannonian and Pliocene sediments are present.

On the entire territory the Quaternary deposits are developed, representing different genetic types from the river terrace sediments in the area of terraces; the gravelly-sandy Danube sediments near Gabčíkovo reach a thickness of approx. 500 m.

PRE-TERTIARY BASEMENT

On the basis of the work of Fusán et al. (1987), Haas et al. (2000) and own interpretation based on new knowledge of wider tectonics of the Western Carpathians, in the setting of Pre-Tertiary basement the tectonic units of the Tatricum, Veporicum, Hronicum and the Transdanubian Mountains (unit Pelsö or Pelsőnia) take part.

The Tatricum rock sequences are represented by crystalline fundament, made of predominantly granitoid crystalline rocks and schists.

The Veporicum unit is located mainly in the southeastern part of the territory. It consists of granitoid rocks, below which mica schists are present. In the area of Pozba, Podhájska and Vráble Mesozoic rocks are present; we affiliate them to the Northern Veporicum envelope. The Mesozoic sequence cropping out in the form of so-called "Levice Islands" is considered to be a part of the Hronicum tectonic unit (Nagy et al., 1998).

In the southernmost part of the territory the wells reached Palaeozoic and Mesozoic rocks belonging to the

Transdanubian Mountains of the Dinarides Province (c.f. Haas et al., 2000). With the units of the Inner Western Carpathians they have a contact along significant tectonic line of Rába - Hurbanovo - Diósjenö (Hurbanovo Fault).

NEOGENE

The oldest rocks are of Middle Miocene age. They are overlain by younger Late Miocene and Pliocene sediments, and besides the Sarmatian deposits none of them have been exposed. Buried volcanic centres are located at the interface of the Pre-Tertiary basement and Neogene sedimentary fill (Figure 4.1.1.2).

According to the data from seismic sounding (Hrušecký et al., 1993, 1996, 1998) the thickness of the sedimentary rocks in the Gabčíkovo central depression is approximately 8-9,000 m.

The figure 4.1.1.2 shows horizons, which due to their lithology can serve for potential CO_2 storage. The problem seems to be the fact that the area is the largest reservoir of potable water in the Central Europe.

In the following text we characterise in detail only stratigraphic sequence of the rocks potentially suitable for the CO_2 storage.

Eggenburgian

The Neogene sequence starts with Eggenburgian clastics; in the Blatné Depression they are represented by Podbranč Conglomerate and in the northern part of the Rišňovce Depression by Kľačno Conglomerate. The Fm. reaches a thickness of up to approx. 50 m. Atop the basal clastics there is a pelitic member - Čausa Fm. (Figure 4.1.1.3).

Karpatian

Early Karpatian coarse-clastic deposits (Planina Fm.) overlay locally the Pre-Neogene surface. In the basinal environment the deposition had continued without interruption from Karpatian to Ottnangian, mostly. A number of recurring graded cycles of conglomerates (breccias)-siltstones-claystones in distal facies development reflects the dynamics of the sedimentary environment. Within the basinal environment siltstones deposited with interlayers of sandstone and claystone (**Lakšárska Nová Ves Fm.**). The maximum thickness of the formation is approximately 700 m (Figure 4.1.1.4).

Badenian

Early Badenian

Marine sediments of Early Badenian age are found in the Želiezovce and Komjatice depressions, where they represent **Bajtava Fm.** (Vass 1989, in Keith et al. 1989). The main mass of sediment is formed by disintegrating grey calcareous siltstones and claystones. Their thickness is about 1,400 m.
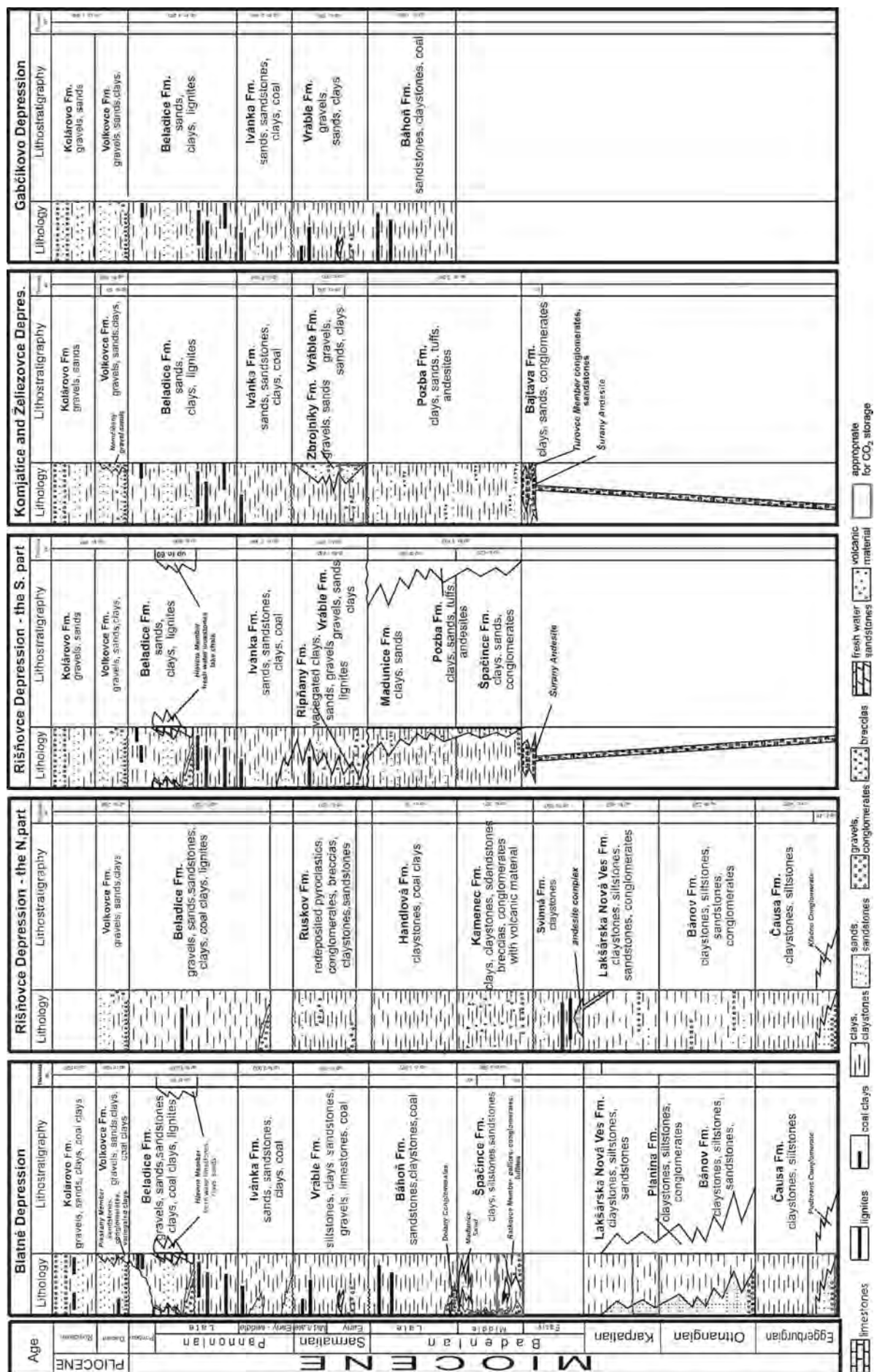
Fig. 4.1.2 Lithostratigraphic column of the Neogene sedimentary fill of the Danube Basin (Nagy 2011).

In the NE part of the Komjatice Depression and the E part of the Želiezovce Depression, ***Turová Member*** underlays the Bajtava Fm. (Vass in Melioris & Vass in 1982), made up of rare quartzose sands with sporadic pebbles of quartz and quartzite, conglomerates and breccias, variegated clays and silts, and andesite tuffs.

The thickness is a few tens of metres (Vass et al., 1980). They occur also in the Bátovce partial depression in the vicinity of PKŠ-1 borehole (Gondovo, Nagy et al. 1998).

In the northern part of the Rišňovce Depression the Badenian sediments are represented by Svinná Fm. made of claystones, sandstones, lignites and at the bottom part by andesite intrusions.

Fig. 4.1.1.3 Distribution of Eggenburgian sediments in the Danube Basin (Nagy, 2011).

Explanatory notes: 1-grey calcareous sandy clays and siltstones with tiny layers of rhyodacite tuff (Čausa Formation) with marginal facies of conglomerate and sandstone (Podbranč and Kľačno Conglomerates), 2-the sediments thickness.
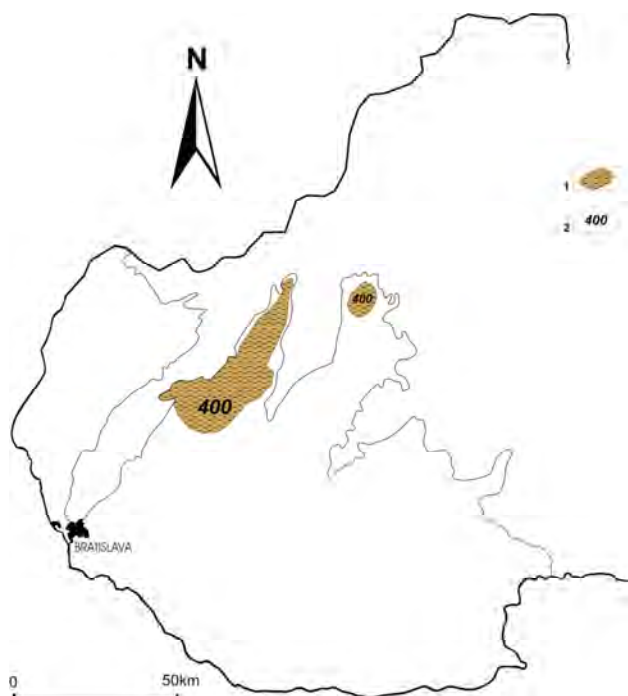
Fig. 4.1.1.4 Distribution of Karpatian sediments in the Danube Basin (Nagy 2011).

Explanatory notes: 1-grey calcareous siltstones, or alternation of siltstones with sandstones of basinal facies (Lakšárska Nová Ves Formation), siltstones and claystones with tuffs (Prietrž Member), distal clastic facies (Jablonica Conglomerate), 2-thickness of the sediments.

Fig. 4.1.1.5 Extent of Badenian sediments in the Danube Basin (Nagy, 2011).

Explanatory notes: Early Badenian: 1-marine sediments of basinal environment with coarse-clastic sediments at the edges - Bajtava Fm.,at the base with continental deposits of Turová Member (Komjatice and Želiezovce Depressions), marine sandy-pelitic sediments - Svinná Fm. (Rišňovce Depression), 2-Šurany volcanites of buried volcanic centres, 3-thicknesses of the Early Badenian sediments, 4-Middle Badenian - marine pelitic sandy sediments - Špačince Fm. (Blatné Depression), bottom part of the Pozba Fm. (Komjatice and Želiezovce Depressions), claystone, sandstone, clays, conglomerates, breccias, with volcanic admixture - Kamenec Fm. (northern part of the Rišňovce Depression), 5-thickness of the Middle Badenian sediments, Late Badenian: 6-marine littoral sediments - Báhoň Fm. (Blatné, Rišňovce Depressions, Gabčíkovo Basin), top part of the Pozba Fm. (Komjatice and Želiezovce Depressions), 7-volcanoclastics of the Burda Fm., 8-thickness of the Late Badenian sediments

In the Danube Basin, below the Middle Badenian sediments (Fig. 4.1.1.5) andesite volcanites of stratovolcanic structure are buried - andesite lava flows alternating

with andesite volcanoclastics. They are widespread in the central part of the basin and also at the western edge of the basin and they are termed as **Šurany volcanites** (Vass 2002). According to boreholes they reach a thickness of 230 to 890 m.

Middle Badenian

In the Blatné and the southern part of the Rišňovce depressions the Middle Badenian sediments are represented by the **Špačince Fm.** basinal facies of grey calcareous clay with shaly slaking (tegel), siltstone and claystone (Jiříček in Papp et al., 1974, Vass, 1989, in Keith et al., 1989). The lower part of the formation (*Ratková Member*) and distal facies are made up of sandstones, conglomerates, rarely organogeneous sandy limestone (*Doľany Conglomerate*).

In the northern part of the Rišňovce Depression Middle Badenian is represented by **Kamenec Fm.**, consisting of clays, claystones, sandstones, conglomerates, locally breccias. They contain a volcanic admixture.

Thanks to their distinctness caused by the presence of andesite and acid volcanoclastics the sediments of the Komjatice and Želiezovce Depressions were included under the common name of **Pozba Fm**. The Formation is typical of conglomerates, sandstones and tuffs on the margins. Towards the Basin basal clastics disappear. Basinal facies represent slaking grey calcareous siltstones and claystones.

Closer to the northern edge of the Basin the Formation is dominated by calcareous, at places sandy claystones and siltstones. According to the geophysical measurements, on the flanks of the Levice Horst, which separates the Komjatice and Želiezovce Depressions, bioherms of algae limestone can be expected (Hrušecký et al., 1996). The thickness of the Formation in the territory studied amounts to approx. 600 m (Fig. 4.1.1.5).

Late Badenian

The Late Badenian sediments are preserved throughout the almost entire Danube Basin (Figure 4.1.1.5). In the Blatné Depression they are represented by the **Báhoň Fm.** (Vass, 2002). They consist of alternating layers of slaking grey calcareous siltstones and claystones with minor sandstone/sands layers (Homola 1951, fide Biela, 1978a; Homola in Homola edit., 1958). On the western edge of the Blatné Depression the upper part of the Formation is made of clays, coaly clays with coal seams 0.8-3 m thick (Vass & Gašparík et al., 1978). The maximum thickness of the Formation in the area studied is 800 m.

In the course of this period, in the northern part of the Rišňovce Depression, pelitic **Handlová Fm.** deposited reaching a thickness of about 10 m. In its southern part clays and sands of **Madunice Fm.** deposited reaching a thickness of approximately 340 m. In the Komjatice and Želiezovce Depressions the referred to above **Pozba Fm.** is present. The total thickness of the Pozba Fm. is approximately 700 m.

Sarmatian

In the Danube Basin the Sarmatian sediments (Figure 4.1.1.6), which were formed at the same time along with the products of contemporary volcanism described above, are represented by the Vráble Fm. (Priechodská et al., 1988).

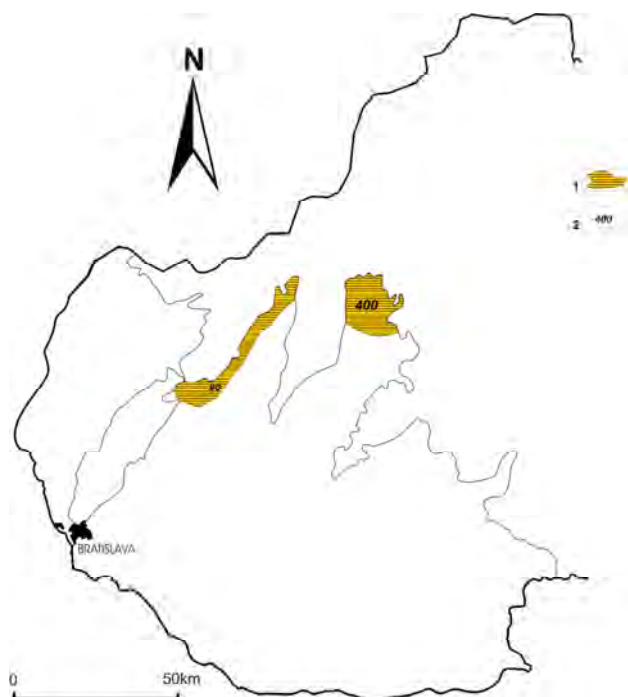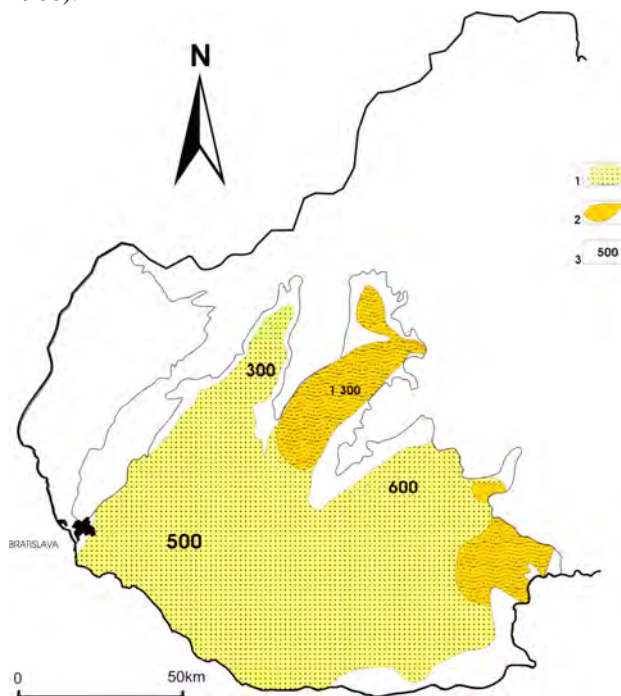*Fig. 4.1.1.6 Distribution of Sarmatian sediments in the Danube Basin (Nagy 2010).*
Explanatory notes: 1-calcareous green clays, siltstones and sands (Vráble Fm.), conglomerate of the distal facies (Doľany Conglomerate), 2-organodetritic limestones, sandstones, acid tuffs, clays, clays and locally coaly clays and tiny seams of coal representing deltaic sediments (Ripňany Fm.), 3-the thickness of the sediments.

The Formation has a varied lithological composition. In the Blatné Depression and in part of the Rišňovce Depression calcareous silts and clays dominate, on the outskirts of the Depression with positions of gravel and organogeneous limestone. The upper part of the Formation consists of sands and clays, variegated clays, coaly clays with lenses and tiny seams of coal (Gaža, 1961, Gaža et al., 1985; Homola et al. (1955, fide Biela, 1978). Mainly at its basis the Vráble Fm. in the Želiezovce Depression is formed of conglomerates, sandy, oolitic and lumachella limestones, and sandstones/sands and acid biotitic tuffs. Towards the centre of the Depression a proportion of grey calcareous, locally tuffaceous clays, is growing.

The total thickness of the Vráble Fm. according to Hrušecký et al. (1996) is 300 m (Želiezovce Depression), 500 or 700 m (Blatné, Rišňovce and Komjatice Depressions).

In the central part of the Rišňovce Depression a subsidence of the Danube Basin resulted in the retreat of the sea to the South. In its northern part the redeposited pyro-

clastics, conglomerates, breccias, claystones and sandstones of the **Ruskov Fm.** were deposited reaching a thickness of approx 120 m.

In the course of the Sarmatian to Early Pannonian in the southern part deltaic freshwater sediments of the **Ripňany Fm.** deposited (Fordinál & Elečko, 2000). At the edge of the Basin finger-like contact with the Vráble Fm. occurs; the sequence is covered by younger sediments. The maximum thickness is 1,430 m.

The Komjatice Depression is dominated by the clays and sands, frequently the tuffaceous ones. They are exposed in the area of the Kozmálovské vŕšky Hills. In the Želiezovce Depression marginal shallow-water sediments of the Vráble Fm. (**Zbrojníky Fm.**) are represented by fine-grained tuffaceous sands and sandstones with interlayers of fine conglomerates, tuffaceous siltstones and claystones. The sediments reach approximately 300 m in thickness.

QUATERNARY

For the purpose of CO_2 storage the Quaternary has no practical meaning, and therefore we do not discuss it.

TECTONICS

The Danube Basin was opened as a result of heterogeneous thinning of the lithosphere. Its evolution started with initial phase of rifting, later continuing with synrift and finally postrift opening phase (Vass & Pereszlényi 1998). The initial rifting phase occurred during the Early and Middle Miocene. The main part of the synrift phase was activated during the Middle Miocene, the postrift phase filled-up the Basin in the Late Miocene and in Pliocene.

For the CO_2 storage **neotectonic evolution** is of particular importance, since this directly affected the integrity of already incurred traps regardless of whether they are filled with hydrocarbons, or not. The neotectonic events and processes that have taken place in the period since the end of the Pliocene, represent the youngest stage of the last tectonic-sedimentary megacycle of the Danube Basin evolution (Kováč & Baráth 1995, Kováč et al. 1997). In conformity with the megacycle beginning, at the same time changed the characteristics of the stress field, which have persisted until recent (Bada 1999).

From the above it can be seen, which fault structures can be expected in the scope of detailed works, which could lead to the potential repository.

If we summarize this fairly detailed entry, so for this purpose are suitable mainly lower members of Eggenburgian (Čausa Fm.), Karpatian (Lakšárska Nová Ves Fm.), Badenian (Špačince Fm.) and Sarmatian (Vráble gravels and sands). Most of these complexes are located in the Blatné and Rišňovce Depressions.

4.1.2 Hydrocarbon deposits in the Danube Basin - local aquifers

The Danube Basin is in compare to the "hydrocarbon more productive" basins (Vienna and East-Slovakian) less demonstrated in terms of production; however, especially in its peripheral parts the structure are existing, that could serve the purpose. They are located in the areas of the municipalities Krupá, Cífer, Báhoň, Trakovice, Sereď and Ivánka - Golianovo (Fig. 4.1.2.1).

They were characterised lithologically and lithostratigraphically with regard to the geological and structural setting of the site. The estimated parameters were sealing structures and the presence of natural gas in the structures or in their superincumbent. The following estimates are based on the dimensions and capacity of the collector lithology, their average or predicted porosity and permeability, taking into account the factor of solubility of carbon dioxide under given conditions. ***We have to note, that unlike the objects in the Vienna and Trans-Carpathian Basins we are dealing with capacities of the local aquifers of the deposits and not the deposits objects.***

Supplementary information provided the calculated natural gas reserves in the superincumbent or in the upper parts of the selected structures. In the case of their extraction new capacities for CO_2 storing would be gained.

4.1.2.1 The Krupá Structure

The structure is located in the north-western part of the Blatné Depression of the Danube Basin (Fig. 4.1.2.2).

It is made up of conglomerates and sandy conglomerates, Eggenburgian in age (Dobrá Voda Conglomerate of the Čausa Fm.), and of Karpatian conglomerates (Jablonica Conglomerate of the Bánovce Fm.), separated by Eggenburgian calcareous claystone interlayer from the Čausa Fm. Both coarse-clastic horizons are water-bearing. These are mineralized aquiferous types of a collector.

On the basis of the work by Gaža (1979) and Biela (1978) the basement consists of Middle Triassic solid dolomitic brown-grey limestones of Havranica type affiliated to Hronicum Nappe. The basal Eggenburgian littoral conglomerates and sandy conglomerates - Dobrá Voda Conglomerate, form planar and thinly-lenticular layers. They reach a thickness of about 60 m and are water-bearing.

They are overlain by neritic clayey facies of the Čausa Fm. in a variable thickness, whereas they gradually wedge out towards the Northwest.

The following base of the Karpatian sediments is made of conglomerates and sandstones of anoxic lagoonal-marine origin, belonging to the upper part of the Planina Fm. (in the lithostratigraphic column of the Danube Basin they are assigned to the Jablonica Conglomerate). They reach a thickness of about 110 m and are water-bearing.
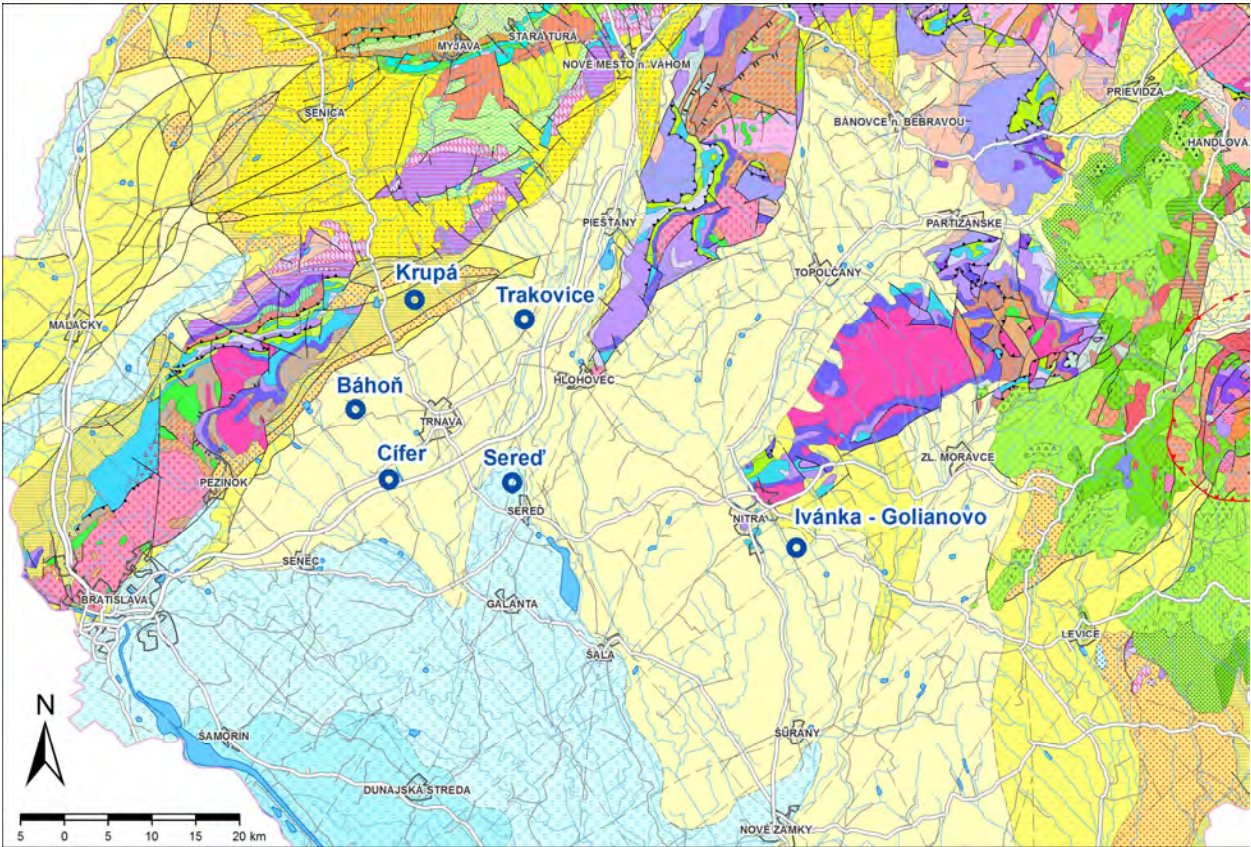
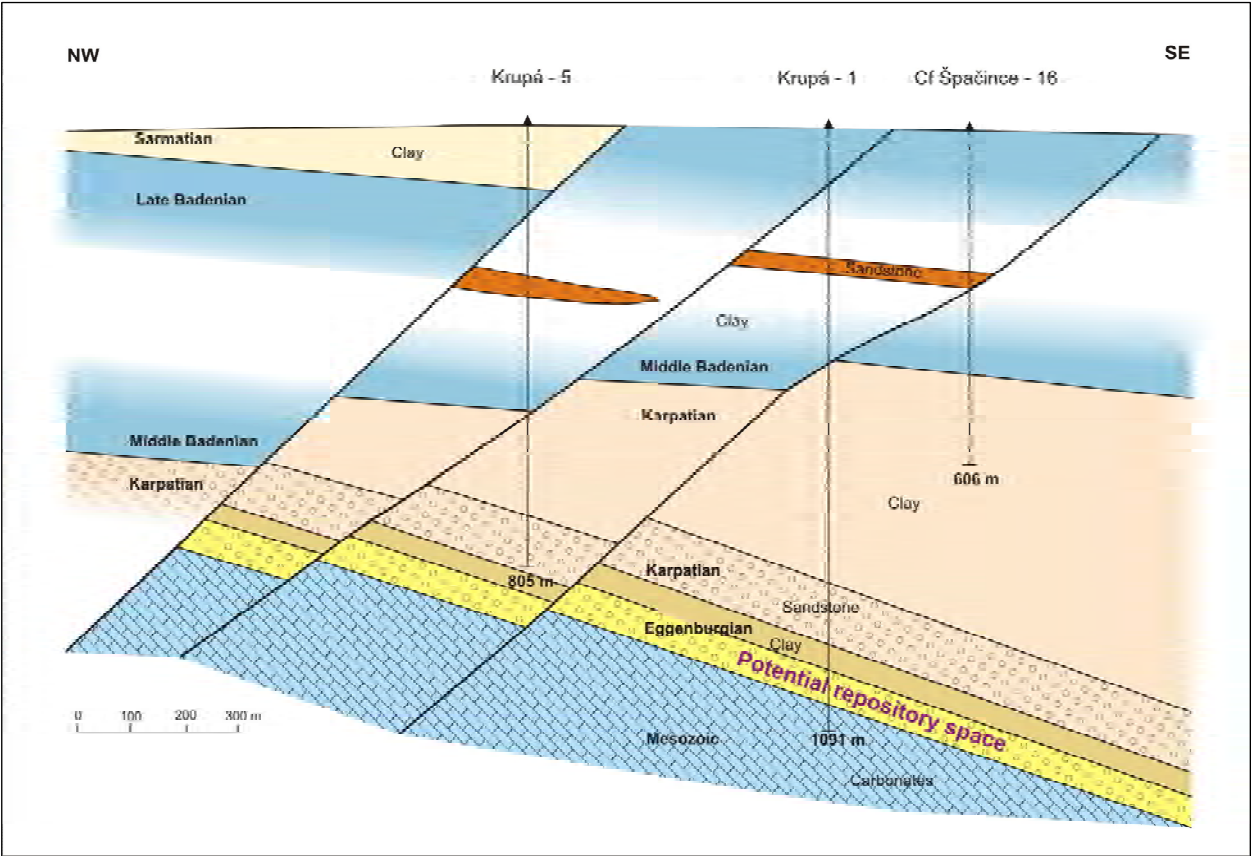*Fig.4.1.2.1 Gas structures of interest in the Danube Basin*

Fig. 4.1.2.2 Geological profile through the Krupá structure (adopted after Gaža, 1979)

They are overlain by Karpatian neritic schlieren facies of aleuritic claystones of the top of the Bánovce Fm. Their thickness here exceeds well beyond 100 m.

Thanks to postsedimentary deformation the sediments form SE inclined slope of a brachysyncline (Pěničková, Dvořáková, 1985). In the North-West it partially restricts the Kátlovce sinistral-normal fault system of WSW-ENE strike with a NNW dip, while on the southern edge the restriction constitutes Dubovany sinistral-normal fault and on the East foot the structure is enclosed by Dechtice normal fault. On the western and northern boundaries erodible wedging out of clastics is likely involved.

The uppermost part of the collector is located at a depth of 600 m and it is inclined with an angle of 15° to the southeast, later steeply up to a depth of about 1,300 meters.

The structure of the collector is of a brachysyncline shape and its top marginal parts are limited due to erosive-transgressive colmatage of Middle Badenian pelitic sediments of the Špačince Fm.

For the sealing parameters of the collector critical are normal faults of the Kátlovce sinistral-normal fault system with a dip to N to NW, it means the direction beneath the Dechtice Block of the northern part of the Malé Karpaty Mts.

Lateral migration of fluids to the northwest through the northern Kátlovce fault, enclosing the structure from the North, is limited by normal fault closure, made of Karpatian impermeable claystones of the top of the Bánovce Fm., and overlying complex of Middle Badenian calcareous claystones of the Špačince Fm.

In the vertical direction the Kátlovce fault system crosses up to 700 m thick complex of pelitic sediments, Karpatian and Badenian in age, which are characterized by good adhesion to the fault plane surfaces.

The sealing nature of the fault zone is well documented by natural gas accumulation in a thin horizon of Badenian sands, high up in the caprock of the collector.

The Krupá structure has an area of approximately 27 800 000 m^2. The average porosity of coarse clastics can be up to 23%. According to different sources of information the formation CO_2 factor for aquiferous type of collector, can vary between 0.02 and 0.30. For the calculation we are prone to adopt the minimum capacity factor.

On the basis of the calculation the capacity of the collector can reach up to 5 294 232 t CO_2 in the 60 m thick Eggenburgian conglomerates and 9 706 092 t CO_2 in 110 m thick Karpatian conglomerates.

The total capacity of the two horizons could thus be 15 000 324 t CO_2.

The value, in spite of the lowest value of the formation factor, is to be understood as the maximum, with no adjustments on the variability in thicknesses, the inhomogeneity in cementation and permeability, etc.

4.1.2.2 The Cífer Structure

It is the elevation structure in the central part of the Blatné Depression of the Danube Basin (Fig. 4.1.2.1). On the basis of the works of Gaža (1994a) and Biela (1978), Middle Badenian water-bearing basal sandy conglomerates overlain by pelitic facies are present here; the sequence belongs to the Špačince Fm. To the collector we can potentially assign the Karpatian Jablonica Conglomerate and sandstones of the top of the Bánovce Fm. (separated from the Badenian conglomerate by schlieren facies of the Bánovce Fm.), as well as the even deeper lying (beneath pelites) conglomerates and sandy conglomerates of undetermined, supposedly Palaeogene age. This is a mineralized aquiferous type of collector. Geological cross-section is presented in Figure 4.1.2.3.

The basement of the Danube Basin in the zone of the aquifer has not been validated by drilling survey; however, it is assumed that is formed by Tatricum crystalline complexes. Basal sandy conglomerates horizon of the Špačince Fm. of Middle Badenian is made of planar and thinly lenticular strata, representing transgressive facies of the western slopes of the Trnava elevation. They reach a thickness of about 60 m and are overlain by neritic clayey facies of the Špačince Fm. with the thickness of over 200 m.

In its basement, the potential collector is separated by a 100 m thick sequence of Karpatian marine aleuritic claystone of the top of the Bánovce Fm. and is made up of 200 m thick Karpatian conglomerate and sandstone of the Jablonica type, a complex belonging to the base of the upper part of the Bánovce Fm. The sediments are likely of alluvial-deltaic origin; upwards they transit into marine littoral facies. They represent a southern marginal base of the Neogene fill of the Danube Basin in this area.

As the next potential collector in the basement we can consider Palaeogene conglomerates and sandstones, separated from the overlying Karpatian conglomerates by a 50 m thick layer of shale. The Palaeogene conglomerates and sandstones are likely of shallow-marine origin and contain a number of thin shale interlayers. They were identified in the borehole Cífer-2, for instance. They where not completely drilled-through; there were encountered only around 130 m of this incomplete core recovery.

The Cífer structure represents a cover of the brachyanticline slope on the western slope of the Trnava elevation (Pěničková, Dvořáková, 1985). In the central area, the upper part of the structure, formed by Badenian clastics, is dipping subhorizontally with a very slight slope eastwards. This situation is due to the tilt of sunken block - in opposite to the Trnava elevation, along the main Trnava normal fault of the NNE-SSW direction, which surrounds the structure at the eastern and southern sides.

From the western side the Cífer structure collector is bounded by another North-South normal Cífer fault, sloping westwards, into the basinal depocentre. In its vicinity the stratification becomes significantly steeper with persisting westward inclination. The northern boundary of the collector is conventionally bounded to isohypse of 2100 m depth of the basin basement; northwards sinks into the larger depths. On the basis of seismic profile in
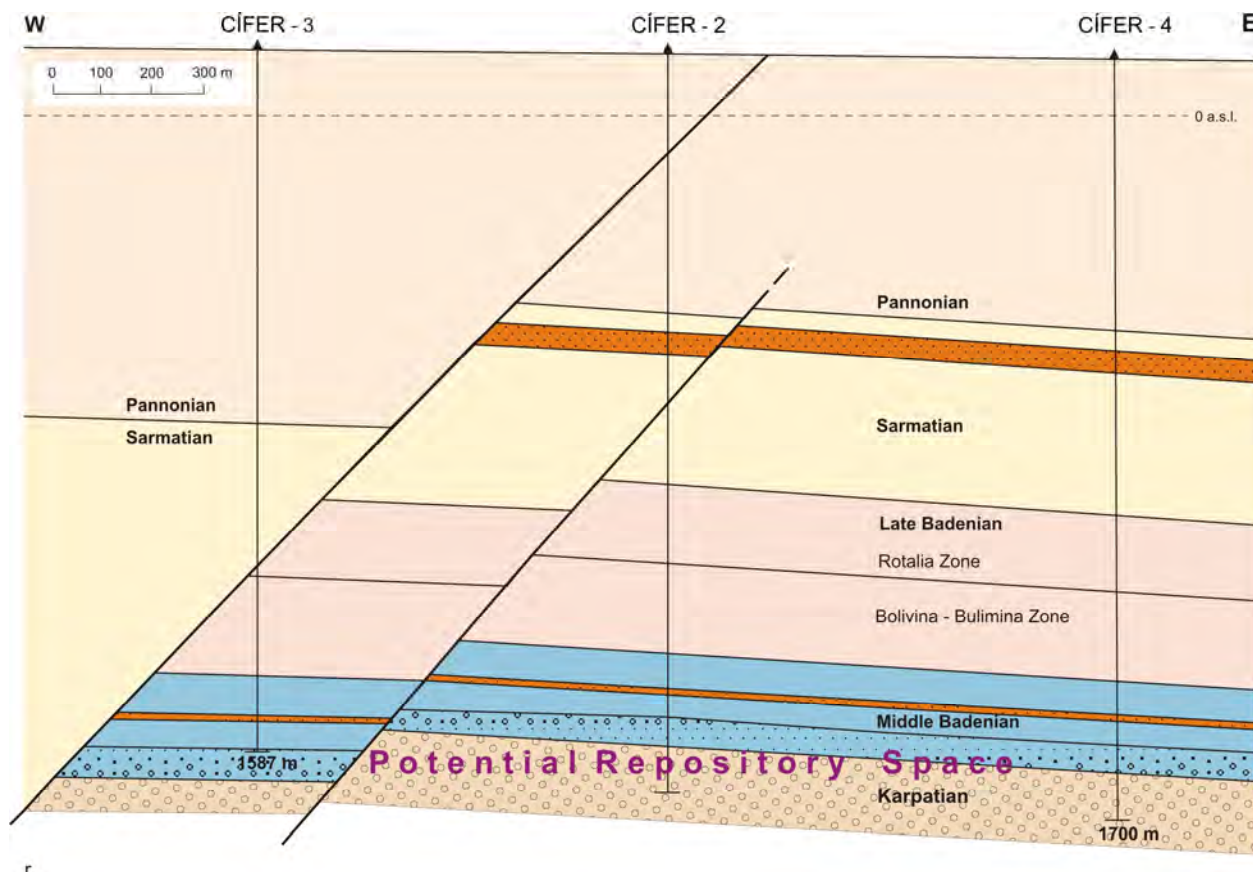
Fig. 4.1.2.3 Geological profile of the Cífer structure (adopted after Gaža, 1994a)

this area (554/77) there is also possible to identify the transverse transpression Cífer fault of the WSW-ENE direction, causing steep southerly arching of the Cífer structure.

The uppermost part of the collector is located at a depth of around 1500 m and drops slightly toward the East. To the West and the North the structure is declining steeply into larger depths.

For sealing parameters of the collector critical are normal faults of the Cífer fault system, restricting the top part of the structure of sunken block, with westerly inclination to the basinal depocentre. Lateral westward migration of fluids through the Cífer faults is limited by normal fault sealing made of impermeable Badenian claystones of the Špačince Fm.

In the vertical direction the Cífer fault system crosses up to a few hundred meters thick complexes of dominantly pelitic sediments, Badenian and Sarmatian in age. They are characterized by good adhesion to the fault plane surfaces.

The sealing nature of the fault zone is well documented by preserved accumulation of natural gas within Middle Badenian and Late Sarmatian thin sandy horizons in the close and more distant superincumbent of the collector proposed.

The Cífer structure has an area of approximately 14 250 000 m^2. Porosity of coarse clastics may be up to 20% on average.

The capacity of the collector in the ideal state of physical properties may be at the minimum formation factor for the aquiferous type of collector about 2 359 800 t CO_2 in the 60 m thick horizon of Middle Badenian age, or 7 866 000 t of CO_2 in the 200 m thick Karpatian conglomerates; finally, a potential of 5 112 900 t CO_2 is assigned to 130 m thick Palaeogene conglomerates.

In sealed and from the aquifer isolated superincumbent of the aquiferous body there are two horizons of porous sandstone containing gas with dominating nitrogen (N_2) (Gaža, 1994a).

The upper horizon is located in the sandstone horizon, Late Sarmatian in age, intercalated within sealing claystone (Vráble Fm.). The thickness of the horizon ranges between 4 and 10 metres; in the borehole Cífer 2 it was identified in a depth of 620 m. Calculated capacity of the horizon is 11.45 million m^3 of natural gas, of which 2.62 million m^3 consists of methane and dominant 8.83 million m^3 is the representation of nitrogen.

In the case of extraction of the balancing amount of ca. 7.6 mil. m^3 of natural gas, it would be theoretically possible to replace the gas in the collector by CO_2 injecting, but due to a small depth of the horizon, the CO_2 storage would not be effective.

A deeper horizon is tied to a relatively thin layer of Middle Badenian sandstone inside a sealing claystone (Špačince Fm.). It reaches a thickness of 4-10 m and in the well Cífer 2 it is identified in the depth of 1,435 m.

Gas reserves were calculated at 66.63 million m^3 of which 15.26 million m^3 involves methane, and 51.37 million m^3 is made up of nitrogen (Gaža 1994).

In the case of extraction of the balancing amount of ca. 44.4 million m^3 of natural gas, it would be theoretically possible to replace a gas capacity of the collector by CO_2 injecting. At the assumed bulk density of CO_2 at the rate of 0.7 $g.cm^{-3}$, the mass of CO_2 could be about 31.1 million tonnes. While applying formation factor of 0.003, the real capacity could reach 93 ths. tonnes of CO_2.

The calculations are approximate, but the structure is a good candidate for a model solution to the technological possibilities of CO_2 storage into depleted deposit space in the form of a pilot program. The question is whether the N_2 reserves are an interesting commodity for a potential customer.

4.1.2.3 The Báhoň Structure

The object is located in the western part of the Blatné Depression of the Danube Basin (Fig. 4.1.2.1). According to the borehole database (Biela, 1978) the object is made of Middle Badenian conglomerates and sandstones at the base of the Špačince Fm. overlying Pre-Neogene basement. Clastic horizons are water-bearing. This is a mineralized aquiferous type of collector. The seismic profile across the site is presented in Figure 4.1.2.4.

The basement of the collector in the southern area, as validated by drillings, is made up of crystalline rocks of the Malé Karpaty Mts. (mainly granitoids and biotitic mica schist gneisses). Middle Badenian basal conglomerates and sandstones of the Špačince Fm. in the borehole Vištuk 2 are of likely alluvial origin on their basis, and upwards they transit into littoral marine facies. The basal conglomerates here reach the thickness of up to 300 m and the sandstones in their direct superincumbent are around 200 m thick. Therefore they represent a gigantic water-bearing collector. In the borehole Báhoň 1 the sequence is not completely drilled-through and only the top part of the marine sandstone-conglomerate collector is recovered reaching a thickness of 220 m with multiple thin claystone interlayers. In their superincumbent, the claystones belonging also to the Špačince Fm. occur again along with sandy claystones of the Madunice Fm., reaching a summary thickness of more than 1000 m.

The Báhoň structure represents a Middle Badenian active segment of the subsiding pull-apart partial depression, filled-up in short period of time by enormous accumulations of coarse clastics, which have not been completely drilled-through by deep survey. In the northern part of the territory in the borehole Suchá 3 they are known in incomplete thickness of more than 500 m in significant depths. Their clastic material is derived from Tatricum units and to the North also from the nappe units of the Malé Karpaty Mts. They overlie probably a dissected Pre-Neogene basement, formed of the Malé Karpaty Mts. Tatricum. They have the nature of depression

fill and its western supplying slope, which is reflected in their depositional geometry - while in the eastern part they are deposited subhorizontally. To the West their stratification is controlled by normal faulting.

According to the structural map (Pěničková, Dvořáková, 1985) in the West the Báhoň structure is restricted by the southern branch of the Boleráz fault of the SW-NE direction, of mostly normal fault nature. In the East, the border of the structure is controlled by uneven Budatín fault of strike-slip mechanism with a strong normal faulting component. Its direction is approximately NE-SW with a dip to the ESE. The western border of the structure is kept very conventionally, at very approximate isobath contours of Pre-Neogene basement of about 1,700 m.

In the borehole Báhoň 1 the clastics collector surface was encountered at a depth of 1,830 m, and in the borehole Vištuk 2 at a depth of 1,780 m (Biela, 1978).

The structure of the collector has the shape of syncline with dissected internal block structure, which is not sufficiently explored in detail. Vertical migration of the fluids in the rock environment is limited by thick clayey sediments cover of the Middle and Late Badenian.

Lateral migration of the fluids in the East is bounded by a tectonic amputation. In the West we assume a similar amputation, which is, however, necessary to verify in more detail with respect to the height of the vertical displacement of the Boleráz fault system. Due to the steep palaeoshore slope of the pull-apart basin we assume wedging out of coarse-clastic facies at the basement isobath of around 1,700 m.

In this case, we can document the nature of the normal fault sealing and preserved contents of methane and nitrogen in marine mineralized aquifer in wells in the area.

The Báhoň structure is characterized by good porosity and water-bearing just at the top of the marine horizon of the collector (ca 150 m), while the lower coarse-clastic members display a significant degree of cementation with consequent drop in their porosity and permeability.

The structure has an area of approximately 64 000 000 m^2. The average porosity of the coarse clastics can reach up to 14%. The capacity of the collector can attain at the minimum formation CO_2 factor for aquiferous collector type up to 18 547 200 t of CO_2 at the estimated 150 m thick sandstone and conglomerate complex.

4.1.2.4 The Trakovice Structure

The structure is located in the eastern part of the Blatné Depression of the Danube Basin (Fig. 4.1.2.1). It consists of sandstones and sandy conglomerates of the Early and Middle Badenian (lower part of the Špačince and Trakovice Fms.) of variable thicknesses with several clayey sandstone and claystone interlayers. The clastic horizons are water-bearing. This is a mineralized aquiferous type of collector. Geological cross-section is presented in Figure 4.1.2.5.

Fig. 4.1.2.4 Interpretation of the coarse-clastics body, appropriate for storage, in the seismic cross-section 555/77 North of Báhoň Village (indicated by green line), (Baráth, 2011)

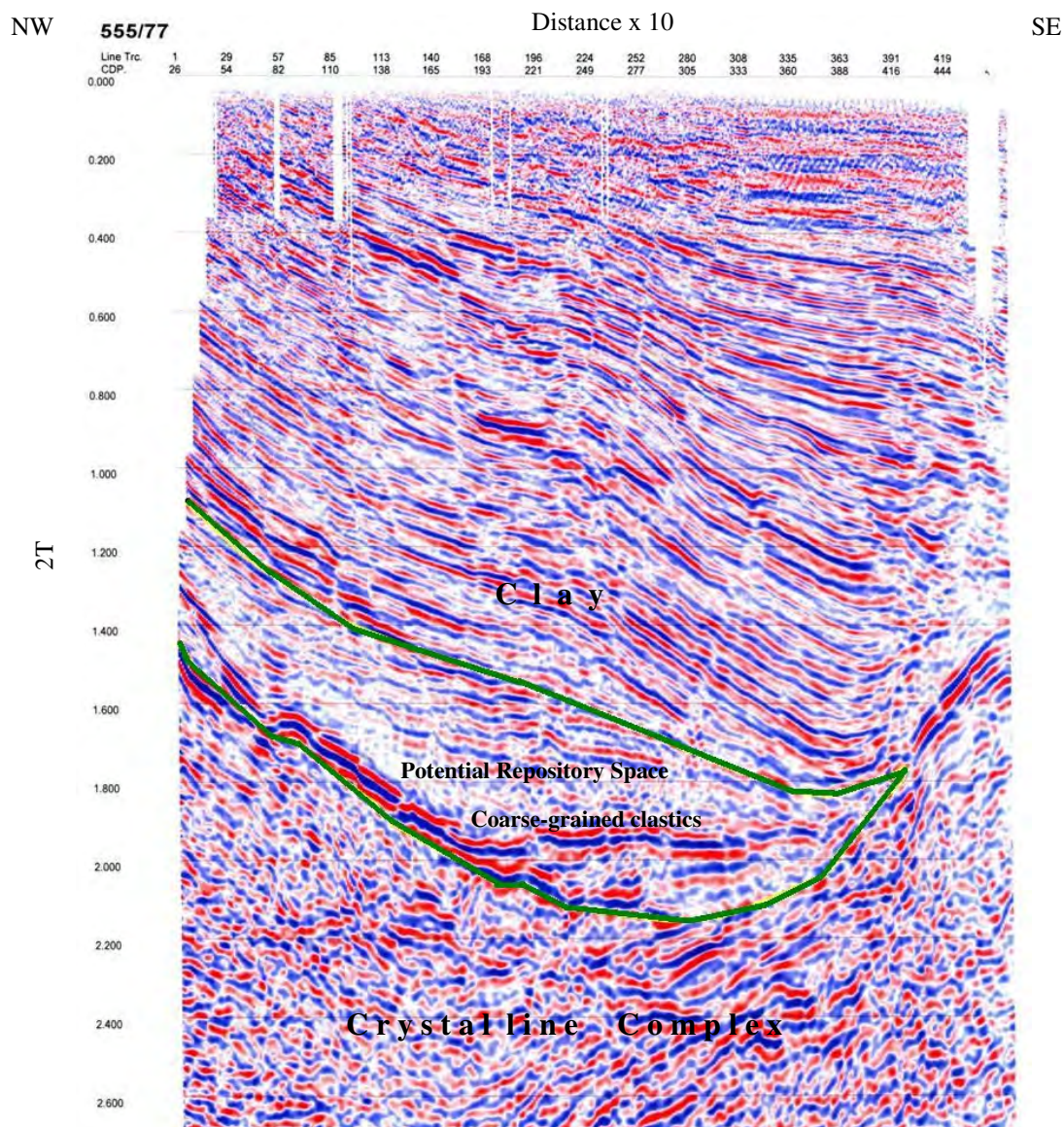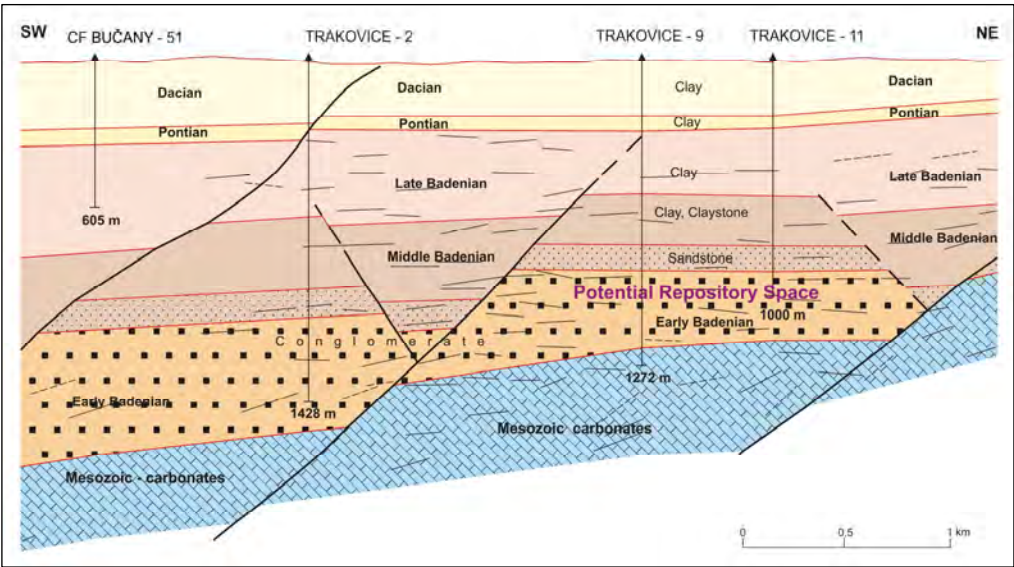*Fig. 4.1.2.5 Geological profile through the Trakovice structure (adapted after Gaža, 1994)*

On the basis of the work of Gaža (1994b) and Biela (1978) the basement consists of Triassic dolomites and dolomitic limestones of Krížna Nappe. Basal Early Badenian sandstones and conglomerates of the Trakovice Fm. are of likely littoral origin and have a variable thickness, depending on the dissection of their palaeorelief. In the Trakovice 3 borehole they reach a thickness of 260 m, including three significant interlayers of claystone with thicknesses of 10, 25 and 55 m, while in the upper part of the borehole Trakovice 9 only the uppermost part of the sequence deposited with a thickness of around 50 m. In their superincumbent calcareous shales are present again belonging to the Trakovice Fm., reaching a thickness of up to 100 to 120 m.

The overlying Middle Badenian sandstones of the bottom part of the Špačince Fm. show signs of deltaic deposition environment and they have frequent claystone and clayey sandstones interlayers. In the borehole Trakovice 9 they reach a thickness of around 200 m, while in the borehole Trakovice 3 the proportion of claystone interlayers is significantly increased, so the sandstone thickness reaches around 70 m in total.

They are covered by neritic claystone facies of the Špačince and Madunice Fms. of a thickness of more than 400 m.

The structure Trakovice represents a cover of the south-western slope of rugged brachyanticline of Trakovice elevation (Pěničková, Dvořáková, 1985). The oldest members of the sequence are found in the deepest parts of the south-eastern part of the structure and towards the North and North-East on the Pre-Neogene basement gradually younger sediments were transgressively deposited. Higher horizons have a subhorizontal stratification with finger-like intrusions of the basinal claystone facies from the West, as well as with the signs of wedging out of sandy horizons in the eastward direction.

To the West the Trakovice structure is restricted by the North-South Trnava normal fault system (t_2) with a western slope and to the East the structure is limited by the other fault of the North-South Trnava normal fault system (t3) with a dip to the West. The northern border of the structure is assumed conventionally at the depth of 1,500 m and in the South the conventional boundaries are also interpreted by a short stretch on the slopes of the transverse elevation of the NW-SE direction, probably tectonically limited.

The uppermost part of the collector in the Northeast is located at a depth of 810-830 m and in the south-western part of the territory its base reaches to the depths of up to 1,800 m.

The brachyanticlinal structure of the collector has a complex internal block construction and has not been sufficiently studied in detail. Vertical migration of the fluids in the rock environment is limited by thick clay sediments cover of the Middle and Late Badenian in the collector superincumbent.

Lateral migration of the fluids is bounded by lithologic wedging out and transition into claystone facies.

For sealing parameters of the collector critical are normal faults of the Trnava fault zone on the eastern and the western edge of the structure.

In the vertical direction the fault system crosses over 400 m thick, dominantly pelitic Badenian sediments complex, which is characterized by good adhesion to the fault planes surfaces.

The sealing nature of the fault zone is documented by preserved small accumulations of natural gas in the horizons of the highest part of the Middle Badenian sands and in the thin sandy horizons in structure's superincumbent.

The Trakovice structure has an area of approximately 18 750 000 m^2. The average porosity of the collector's clastics can reach up to 14%. The capacity of the collector at the minimum formation CO_2 factor for aquiferous collector type can attain at an average thickness 115 m of the clastics complex of Early Badenian age 4 165 875 t CO_2 and at an average thickness of 135 m of the Middle Badenian clastics 4 890 375 t CO_2.

The total capacity of the two systems could thus achieve 9 056 250 t CO_2.

4.1.2.5 The Ivánka - Golianovo Structure

The structure is located on the western slopes of the Komjatice Depression of the Danube Basin (Fig. 4.1.2.1). It consists of Sarmatian basal sandy conglomerates and sandstones of the Vráble Fm. The sediments reach a thickness of about 60 m and are covered mostly by neritic clayey facies of the Vráble and Ivánka Fms. of a great thickness, reaching almost 1800 m (boreholes Ivánka I-2, 3, 6 and Golianovo G-1) (Biela, 1978, Šályová and Mojžiš, 2002). This is a mineralized aquiferous type of the collector with gas "caprock". The basement of the Danube Basin in the area of proposed collector is formed by the Palaeozoic crystalline Tatricum rocks of the Tríbeč block. Basal sandy conglomerates and sandstones form lenticular layers and represent alluvial-fan facies on the south-eastern slopes of the Tríbeč mountain range. The Ivánka - Golianovo structure is a normal fault-restricted Early-Sarmatian alluvial-deltaic body along the Mojmírovce fault of the SSW-NNE direction, accompanied by antithetic fault, crossing the structure. The layers are deposited with a slight dip toward the West-Northwest and the clastics gradually transits into marly facies laterally.

The uppermost part of the collector is located at a depth of about 1,750 m with the base at a depth of around 2,080 m. For collector's sealing parameters the Mojmírovce normal fault is of utmost importance. However, a good sealing against vertical migration of fluids is ensured by overlying clay complexes.

The sealing nature of the Mojmírovce fault zone is well documented by the preserved accumulations of natural gas in the top parts of the Early Sarmatian mineralized aquifer.

Geological cross-section is presented in Figure 4.1.2.6.
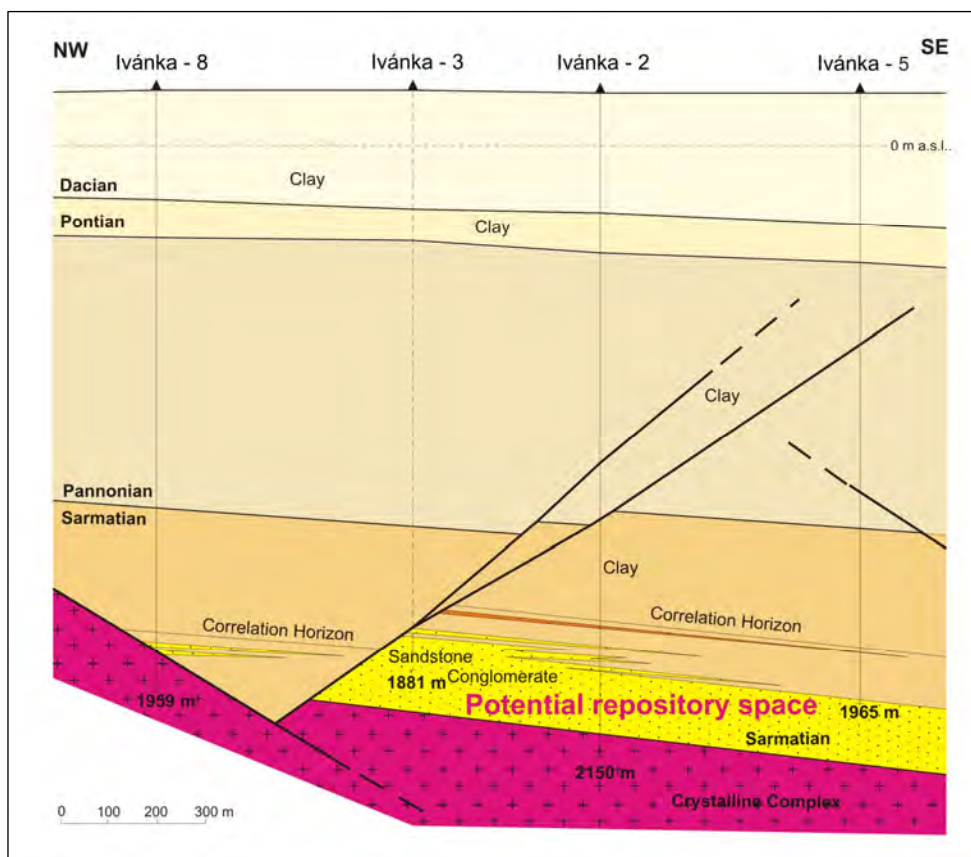
Fig. 4.1.2.6 Geological cross-section through the structure Ivánka - Golianovo (adopted after Šályová and Mojžiš, 2002)

The structure Ivánka - Golianovo has a minimum area of approximately 12.5 km^2. The average porosity of coarse clastics may be up to 12%. The measured permeability of the collector is considerably variable, reaching a maximum of 20 mDa. For an estimate of the capacity of the collector, we used the minimum value of the formation factor.

On the basis of the calculation, the collector's capacity in the ideal state of physical characteristics may be at the minimum formation CO_2 factor for the aquiferous type of collector up to 4,140,000 t.

At the top and the peripheral parts of the structure there have been identified a total of 5 gas-deposit horizons (borehole Golianovo 1 (1999) - operated deposit Ivánka pri Nitre, ENGAS s.r.o. Bratislava, Šályová and Mojžiš, 2002). This is a sandstone-conglomerate collector at the base of Sarmatian sediments of the Vráble Formation.

The 1st up to the 4th horizons are made up of sandstones with the thickness of 2-13 m and the 5th (bottom) horizon is made up of water-bearing sandstones and conglomerates with a thickness of up to 71 m. The upper part of the horizons is sealed with claystones, while in the lower part of the 5th horizon the water/gas boundary was detected inside the clastics at a depth 1695 m.

The total capacity of the collectors was calculated to 1,160 million m^3, of which 0.416 million m^3 consists of methane with ethane ($C_2H_6 + CH_4$), 0.438 million m^3 consists of CO_2 and 0.305 m. m^3 constitutes nitrogen N_2.

The bulk of the reserves (91%) is tied to the bottom 5th horizon.

In the case of extraction of the balancing amount of ca. 733 million m^3 of natural gas, it would be theoretically possible to replace a gas capacity of the collector by injected CO_2. After calculating the bulk density the overall exchangeable mass will reach ca 513 mil. tonnes CO_2. After application of the formation factor 0.003 the capacity of the stored CO_2 is balanced to 1,539,000 tonnes.

4.1.2.6 The Sereď Deposit

(UGSF Križovany nad Dudváhom - Underground Gas Storage Facility)

The deposit is located in the Danube Lowland, North of Sereď, where it was detected by pioneer survey on the structure of Križovany. The deposit is bound to the base of Middle Badenian in the depth of 960-1,060 m (Lorenc, 1968). Its location is depicted in Figure 4.1.2.1.

This is the semi-arch, brachyanticlinal structure, interrupted by Majcichov fault of the ENE-WSW direction. The brachyanticline structure evolved due to arching of the Pre-Neogene basement, encountered by drilling at a depth of 1,385 m. This elevation element presents a continuation of Abrahámovce elevation, which has the general N-S direction.

In terms of facies development the main collector horizon is variable in both the horizontal and vertical directions. It is made up of partly cemented weakly- to
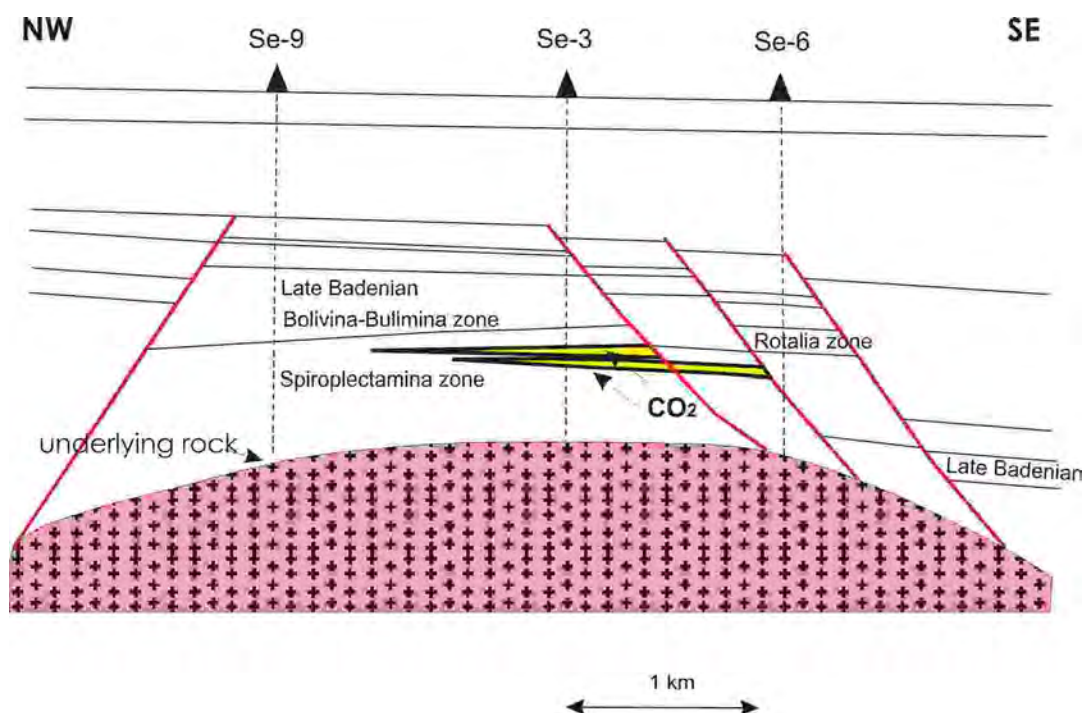
Fig. 4.1.2.7 Geological cross-section through the deposit Sereď (in yellow) (According to Gaža, 1994)
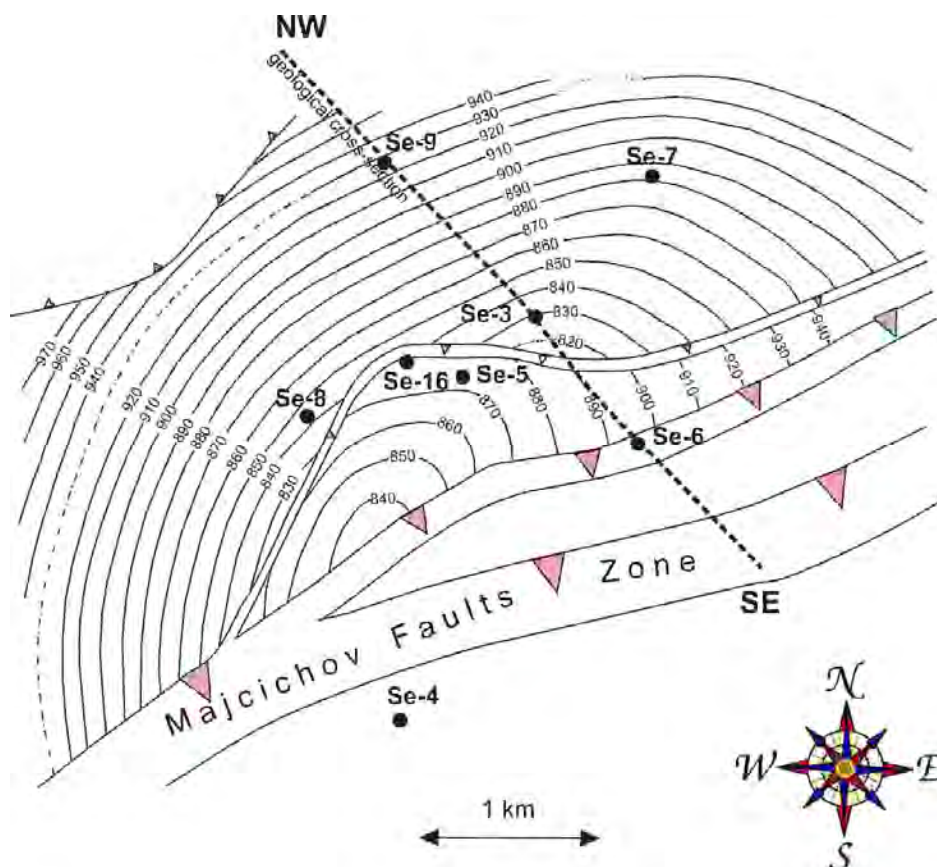
Fig. 4.1.2.8 Structural map of the Sereď deposit with the isobaths of the deposit cap (According to Gaža, 1994)

moderately calcareous sands, with numerous intercalations of calcareous shales, tuffites, tuffaceous sands and sandstones. According to the interpretation of sounding records it is essential, that the upper part of the collector (max. thickness 56.5 m) is permeable, the average porosity is 27%. The deposit water is strongly mineralized, of alkali-haline, sodium-bicarbonate type with summary mineralization of 28.88 g.l^{-1}. In the calculation of reserves its considerable extent was accounted for. The deposit water is saturated by carbon dioxide. In 1994 the original calculation was converted to a new category within the meaning of the legislation, when there were

established (Gaža, 1994) reserves (CO_2 + N_2) in the volume of 4,716 billion m^3. The exploitability coefficient was estimated at 0.7 ratio. The gas composition is as follows: CO_2 = 82.7%; hydrocarbons 6.6%; nitrogen 10.7%; the deposit pressure 11,7 MPa; deposit temperature 57°C; the share of hydrocarbons 314.8 million Nm^3. The adverse gas composition was the reason for further exploration had halted and the NE restriction of the productive zone has not been verified.

From the above it is clear that in the deposit the volume of almost 5 billion m^3 of potential capacity for storage is available in theory.

The hermetic sealing of the deposit was disrupted by the eruption of gas, water and sandy material on the borehole Sereď-3 situated in the top part of the deposit in the sixties of the last century. The uncontrolled emission occurred in the course of gas-bearing horizon testing, when the attempt to stop the pumping test had failed. There was a gas evasion outside column casing rig and the drilling fluid was over-gassed. In the place of the borehole a crater evolved with subsequent collapse of the head-gear. In 1968 on the spot was a circular crater with a diameter of about 20 meters, filled with water with a table level of 1 m below the then terrain with gas gurgling slightly through the water. In the wake of this event the deposit structure has not been recommended for underground storage of gas (Lorenc, 1968).

The deposit should be exploited in order to work out the gas in the Vienna Basin (deposit Vysoká) 40 years ago. An annual production of 500 million Nm^3 gas was foreseen. Today, we are in a different situation, though we don't need to work out a natural carbon dioxide, as it is contained in exhaust gas emissions in a variety of industrial works, but already in the previous period there arose the intentions, which have been revived again today - to take advantage of the deposit for underground storage of natural gas. This would be probably the biggest reservoir in the territory of the Slovak Republic. The question remains - what to do with the dominant CO_2 in the deposit, because the share of the gas methane is almost irrelevant. The deposit can therefore serve as **a natural analogue**, simulating the CO_2 storage, where it would be possible to monitor all the necessary parameters affecting the safe operation of the disposal facility in terms of its hermetic sealing. The deposit meets the criterion of a great depth, providing supercritical status of the gas, along with the corresponding temperature.

At present, the hermetic sealing of the repository has been reviewed and the business plans intend to use it as an underground reservoir. An open question remains where to place the natural CO_2. In the last two years we have not recorded any progress in this activity.

4.1.2.7 The Marcelová Structure

This undoubtedly interesting structure was found within the framework of basic research of geothermal resources of the Komárno High Elevated Block in the

seventies of the last century (Remšík, et al., 1979). A follow-up search survey (Klago and Tyleček, 1988) brought the amount of knowledge that we have summarized, for the purposes of the task, in the following text.

Pre-Tertiary basement of the Komárno Elevated Block

Fusán et al. (1971) defined in the Pre-Tertiary basement of the Danube Basin the Komárno Elevated Block. Its boundary was later (Fusán et al., 1987) specified within the area between Komárno and Štúrovo in the South and restricted by the course of the Hurbanovo fault in the North.

The geological and hydrogeothermal characteristics

According to regional geological division the area of interest is situated in the SW part of the Želiezovce Depression and in the eastern part of the Gabčíkovo Depression (see Fig. 4.1). From the practical reasons we use a tectonic division, which is utilised in the exploration for oil and gas and is presented in Fig. 4.1.2.9.

The Komárno Elevated Block represents a tectonically strongly affected territory, where Mesozoic was encountered at various depths, ranging from tens of meters to 1 km below the surface. As it has been observed from deep boreholes, there were encountered the rocks in the range of Triassic sediments till the Cretaceous ones. From the Palaeogene sequences there were identified Eocene and Oligocene in the area of Modrany (NE of the site). The Neogene sediments of variable thicknesses in the wider surroundings of the site are present in the stratigraphic range from Badenian till Romanian, comprising dominant sandy and clayey sediments. In the youngest members gravel is also present. The characteristics of this important phenomenon in this regard have been displayed in the Atlas of Geothermal Energy in Slovakia (Franko, et al. 1995). The Mesozoic carbonate rocks present in the Neogene basement represent a major and important hydrogeologic structure of the thermal waters. Triassic limestones and dolomites are collectors with fissure and karst-fissure permeability. In the Komárno High Elevated Block we distinguish the High Elevated Block itself and a Marginal Elevated Block; they differ in hydrogeothermal conditions, physico-chemical properties of thermal waters, as well as the values of geothermal gradient. Borehole GTM-1 is located in the Marginal Elevated Block (see Fig. 4.1.2.10), encompassing the High Elevated Block from the West, North and East.

As the infiltration areas of the thermal waters are considered the Mesozoic carbonate complexes of the Transdanubian Mountains, exposed on the surface on the right bank of the Danube in the Vertes, Gerecse and Pilis mountains.

According to the geophysical data (Zbořil, et al., 1988) the territory is segmented into number of partial blocks, of the directions NE-SW or NW-SE, with dis-
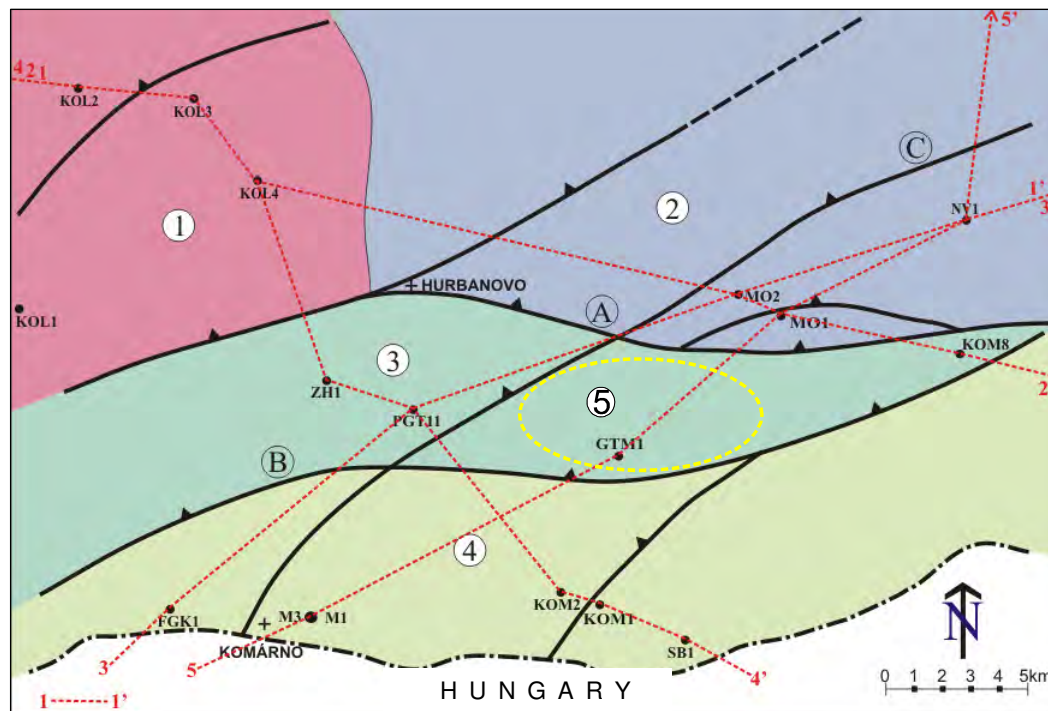
Fig. 4.1.2.9 Tectonic classification of the south-eastern part of the Danube Basin 1-Kolárovo elevation, 2-Dubník Depression, 3-Komárno Marginal Elevated Block, 4-Komárno High Elevated Block, 5-studied area, A-Hurbanovo fault, B-Komárno fault, C-Nové Zámky fault, 1-1' geological cross-section (adopted after Franko, et al., 2011)

placement amplitudes of 50-300 m. Of a number of indications for the geothermal borehole purpose the territory of internal block was chosen between the villages of Modrany and Marcelová, which is represented by Dacian sediments on the surface. The geothermal borehole GTM-1 location is evident from the Figure 4.1.2.9. The borehole was drilled in 1987 with a designed depth of 1 800 m, the actual depth was 1,763.5 m. The borehole identified two hydrogeological structures of geothermal waters in the Mesozoic complex (Klago, 1988):

First depth   1,035.0-1,197.5 m
Second depth 1,405.0-1,760.0 m.

The groundwater is highly-mineralized - 90 $g.l^{-1}$; the yield is 8.33 $l.s^{-1}$. The Na-Cl type water contains higher levels of iodine, bromine, lithium, strontium and metaborite acid. The temperature at a depth of 1,760 m was 65 °C, on the mouth of the borehole it reached 56 °C. In addition, it was also identified a shallower hydrogeologic structure at a depth of 700-723 m, with the yield of 1.66 $l.s^{-1}$ and mineralization of 0.82$g.l^{-1}$, of the type Ca-Mg-SO4-HCO$_3$, however, this is outside of our scope of interest. The drilling profile is shown in Figure. 4.1.2.11.

Klago (1988) notes, that the borehole GTM-1 has not documented the sequel of the hydrogeological structure of thermal waters from the area of Patince towards the Marcelová area. The rational use of this resource has been evaluated negatively.

In 1998, it was elaborated "Calculation of reserves of mineralized J-Br water in the hydrogeological structure Marcelová" (Januš and Kandera), where the volume of

Fig. 4.1.2.10 Geological borehole profile GTM-1 (Marcelová) (modified by Jezný, et al., 1988)
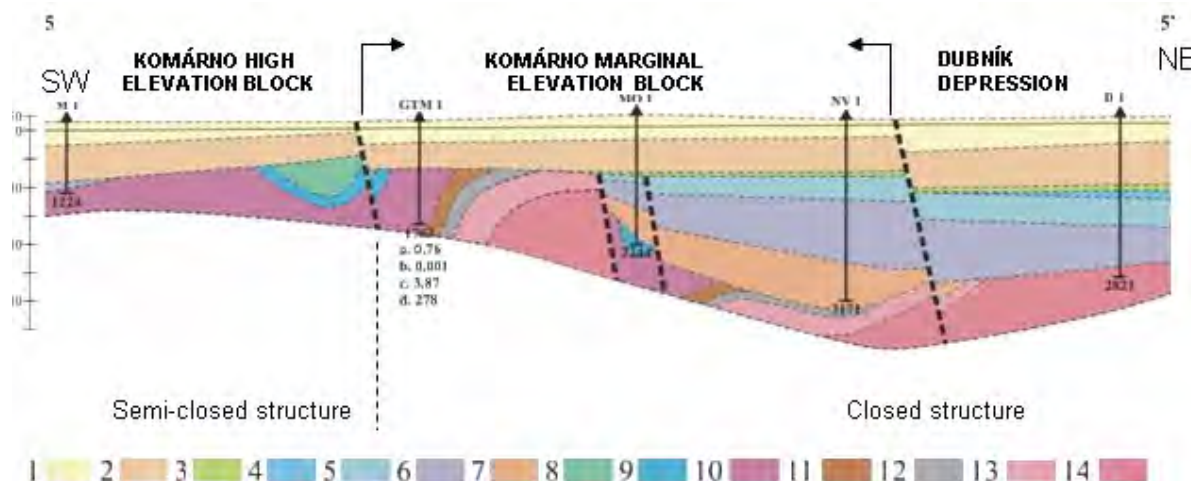
Fig. 4.1.2.11 Geological-hydrogeochemical cross-section through the area of interest.
1-Pontian and Dacian, 2-Pannonian, 3-Sarmatian, 4-Late Badenian, 5-Middle Badenian, 6-Early Badenian, 7-Palaeogene,
8-Cretaceous, 9-Jurassic, 10-Triassic, 11-Permian, 12-Carboniferous, 13-Early Palaeozoic (Devonian), 14-Veporicum Crystalline,
a-rNa+rK/rCl, b-rHCO₃/rCl, c-rNa+rK/rCa+rMg, d-Cl/Br (after Franko, et al., 2011)

1 892 000 m³ estimated reserves were quantified. According to the following calculation (Jezný and Januš, 1988) there were calculated reserves under the terms of the exclusive deposit exploitability, it means according to the reserves economic suitability classified as balance reserves of mineralized waters with the contents of the iodine and bromine salts in the volume of 3 658 176 000 litres, which in 90 g.l⁻¹ mineralization represents 329,236 tonnes of raw mineral material. After the calculation, according to the results of physico-chemical analysis it is possible to determine the amount to 84.14 tonnes of iodides and 724.32 tonnes of bromides. In the permanent extraction of 5.88 l.s⁻¹ of water from the borehole the reserves of mineralized waters are sufficient for a period of 20 years.

The water samples from Mesozoic rocks of the borehole GTM-1 within the meaning of hydrochemical field chart belong to the Na-Cl type, which corresponds to the **closed structure**, in which no endogenous CO_2 evolves and it stores **fossil water**. The cross-section through the structure is depicted in Fig. 4.1.2.11.

The knowledge for the CO₂ storage

From the above established facts and knowledge the following conclusions and proposals of the CO_2 storage can be formulated:

a) facts

– Highly-mineralized water is located in the tectonic internal block Marcelová, on the border of the Western Carpathians and the Pelső unit - encountered by the borehole GTM in the Early Triassic of this unit in depths of 1,037.5-1,045.5 m and 1,739.5-1,761 m. The total thickness of the water-bearing layer is 29.5 m.

– High mineralization from 90 g.l⁻¹ due to Na-Cl water with higher levels of iodine (11 mg.l⁻¹) and bromine (190 mg.l⁻¹), pH 6.1-7.2, satisfies the conditions of the reserves exploitability for the exclusive deposit Marcelová, which is classified as economic deposit (free) with calcu-

lated iodides reserves in the amount of 84.14 tonnes and 724.32 tonnes of bromides (Jezný & Januš, 1998).

– Within the meaning of the chart of hydrogeochemical field the waters correspond to closed structure, in which no endogenous CO_2 evolves - these are fossil waters. Such waters represent I, Br rim of oil terrains, in which the parent hydrocarbon volatilized and the brines are residual fluids.

– The structure is closed, despite the carbonate surroundings - see high mineralization and the borehole GTM-1 did not affect the hydrodynamic regime of boreholes in southerly-situated Patince - the distance of about 5-6 km. This finding is very unique in this kind of geologic environment.

– The reserves of mineralized water have been calculated in the category Z3 in volume 3 658 176 m³. The reserves are classified as the economic ones, free.

b) output into the CO₂ storage issue

– The depths of both horizons are sufficient for achieving the supercritical state of CO_2 (7.38 MPa, 31.1°C), because both of them are at a depth of over 1,000 m. This is evidenced by the measured temperatures of 65°C and pressures at the end of the drill: the pressure at a depth of 1,300 m was above 12 MPa.

– The structure's tightness is an **excellent** argument for the potential repository, because a high level of reliability is assured in terms of leaks. Under keeping the criteria for the pressure of the injection mode the only possible escape routes from the structure are the boreholes, either the injection or the monitoring ones. Permanent decrease in the yield or static pressure values in time also points out to the fact that it is closed hydrogeologic structure (Jezný, et al., 1988).

– Despite the fact that the object is located in a seismically very active zone in Slovakia, this aspect has so far had no impact on its integrity, because they have not been observed any escapes from the reservoir.

– Taking into account the density of the carbon dioxide and formation factor the calculated volume of groundwater reserves for a particular depth at applied volumetric approach in the calculation of the storage capacity allows us to assume the storage of about 70 M tonnes of CO_2, which is the amount sufficient even for the industrially used repository.

– Geochemical modelling of CO_2 suggests that there will occur a solubility trapping. In brine there will be dissolved 0.39 mol.kg^{-1} of CO_2. The water will become aggressive and will dissolve mainly the carbonate mineral phases, with consequent change in saturation indices and likely mineral phases will become under-saturated. This will increase the effective porosity, and thus the increase in the storage capacity, in theory, - the effect of residual trapping and, later, mineral carbonatization, due to the extension of the storage space. (See Chapter 5.1 Geochemical aspects of the storage).

– The above points are very positive in terms of the safety of the repository, because due to foreseen trapping it would not occur an increase in the CO_2 pressure in the reservoir, but the CO_2 will sink to the bottom of the aquifer due to its heavier bulk density.

– The added economic value to CO_2 storage are increased concentrations of iodine and bromine - calculated iodides reserves 84.14 t and bromides 724.32 tonnes (Jezný, et al., 1988). If we compare this with the current prices on the world market (June 2011) the approximate value ranges between 3.5 to 4 million USD. The next value added is the water temperature, which reaches from 63 to 65.5 °C within the intervals of interest and can therefore be used for agricultural or curative purposes, because the waters of this type are scarce (spa Číž as the only region with this type water suffers the lack of replenishment). The assumption of the life of the structure is 20 years, under the operational withdrawal of 5.88 l.s^{-1}.

– In practice, this would mean that by the progressive extraction of brine the space for the stored CO_2 would be gradually emptied.

– This aspect would undoubtedly economically benefit the costly storage of CO_2.

– In theory, as a source of CO_2 injection the emissions of the big producers of CO_2 in the optimum distance from the structure, for example, Duslo Šaľa (approx. 50 km) with an annual production of 500,000 t/year, which produces CO_2 emissions with high purity (99%) are of interest and the only necessary technological adaptation is its compression for the purposes of transport.

Conclusion

The structure has a number of positive features, and not only from the point of view of the projected level of safety of the geological repository, but also provides an economic opportunity to use aquiferous water as a commodity, which is currently scarce on the market. The only Slovak spas - Číž with this type of mineralized water

have significant problems with the insufficient capacity of the source.

The deposit is classified among the exclusive deposits "Marcelová - mineralized I-Br waters"; however, its production is not foreseen in the near future. If we assume that the storage capacity which is derived from the calculation of the reserves is overly optimistic, even at the 50% reduction of the structure parameters the potential repository should satisfy industrial CO_2 storage. In any case, it is referred to as a serious candidate for a potential pilot project structure, which in the case of positive findings could be extended to industrial scale.

Note: Further results with focusing in the hydrogeochemic aspects are presented in the Chapter 5.1 Geochemical aspects of CO_2 storage.

4.2 Zlatá baňa - Slanské vrchy Mts.

The original intent of a search of the appropriate structures for underground CO_2 storage has been focused primarily in the sedimentary complexes of Neogene, Palaeogene, or Flysch, or where there is a presumption of "relatively more favourable" rocks with the required lithologic-tectonic and reservoir characteristics. A summary study of porosity we focused in the rock complex, which from the first point of view is perhaps a bit "odd", but the found parameters, as well as consultations with the responsible staff involved in research work in the area of base metal deposit of Zlatá Baňa in the Slanské vrchy Mts. caused, that we have carried out a more detailed analysis of this site for the purpose of the project.

A Zlatá Baňa andesite Stratovolcano is the most extensive volcanic formation in the northern part of the Slanské vrchy mountain range. It represents a typical conical structure with a diameter of 10 km. The Volcano was named after the village of Zlatá Baňa and is made up of the homonymous formation. In its structure it is possible to allocate the central, transitional and distal volcanic zones. The Zlatá Baňa Stratovolcano represents a range of petrographically differentiated rocks. From the stratigraphical point of view it is assigned to the Early Sarmatian to Early Pannonian periods. The Zlatá Baňa Stratovolcano volcanism products overlie Palaeogene deposits of the Inner Carpathian Palaeogene basin and Karpatian-Badenian sediments of the East-Slovakian Basin (Kaličiak, et al., 1991).

The Pre-Neogene complexes are not exposed in the territory of interest. According to data from deep oil-boreholes Prešov-1, Kecerovské Pekľany-1, Hanušovce-1 and Vranov-1, where these complexes were encountered, the presence of Hronicum is assumed (Grecula, et al., 1980, Tözsér, 1983). According to Pospíšil and Kaličiak, (1978) in the basement of the volcanic complex interferes Humenné Mesozoic.

The deposit of base metal ores Zlatá Baňa (Pb-Zn-Cu + antimonite and cinnabar) evolved in the form of short, steeply-inclined veins and stockworks, accompanied by the impregnations within the hydrothermally-altered

Legend

- Quaternary undivided
- andesite Makovica Stratovolcano, undivided - Early Sarmatian - Early Panón
- andesite Zlatá Baňa Stratovolcano, undivided
- andesite Šťavica Stratovolcano undivided
- andesite Šebastovka Volcano
- extrusive domes, Brestová Fm. - Middle Sarmatian
- epiclastic breccias, Brestová Fm. - Middle Sarmatian
- andesite intrusions
- rhyolite tuffs (Rankovce) - Early Sarmatian
- andesite Stratovolcano Ošvárska – Late Badenian, Early Sarmatian
- siltstones and claystones undivided - Early - Middle Badenian
- calcareous claystones
- Hrabovec rhyodacite tuffs, Early Badenian
- polymict conglomerates
- green-grey claystones in prevail, Kladzany Fm. - Karpatian
- siltstones, claystones, montmorillonite clays, Teriakovce Fm. - Karpatian
- Palaeogene undivided
- faults
- projection of rhyolite horizons at the surface
- cross-sections

Fig. 4.2.1 Geological situation of the Zlatá Baňa area (adopted after Kaličiak et al., 1991)

breccias and is located in the central zone of the Zlatá Baňa Stratovolcano. The deposit has been the subject of intense exploration in the second half of the 20th century (Divinec, et al., 1985, 1989). We would like to avoid repeat the data, we will focus only on the characteristics which are interesting for the objectives of the solved task. Geological map of the site is presented on the modified figure. 4.2.1

In the study of porosity of the volcanic complex rocks we have note quite high values of rhyolites and andesites. In the context of the presented geological setting in geological cross-sections (Kaličiak, et al., 1991) the idea of a potentially possible imposition of carbon dioxide in this space has gradually begun to develop. The following input factors have led us to this concept:

– The volcanic activity in this space started with the eruptions of rhyolite volcanism, when the prevailing rocks were different types of rhyolite volcanoclastics. This activity is dated to the Karpatian period and its products were deposited upon the sedimentary members of the Prešov Fm. - siltstones and sandstones belonging to Eggenburgian (Figs. 4.2.2, 4.2.3). In the superincumbent of the volcanic complex, which is considerable thick - around 500 m - and off the Central volcanic zone it gradually wedges out, once again a sedimentary member - green-grey siltstones and claystones, are developed with horizons of montmorillonite clays that are assigned to the Teriakovce Fm. Above them there are again products of the rhyolite volcanism, although in comparison with the

aforementioned horizon, their thickness and spatial extension are obviously smaller - their maximum thickness does not exceed 300 m. From the morphological point of view both horizons create in fact anticlinal structure. The spatial expansion of both rhyolite horizons is documented in figures 4.2.2 and 4.2.3. In the superincumbent of the higher lying horizon there is again a sedimentary complex of the Kladzany Fm. - green-grey aleuritic shales in prevail over sandstones. Both rhyolite horizons, as well as Kladzany Fm., are dated to Karpatian.

– Atop the volcano-sedimentary complex there is developed a horizon of rhyolite volcanism products - mostly rhyolite pumice tuffs (Badenian). Its dimensions as well as the thickness are the smallest of the all rhyolite horizons. It is sealed by cover of calcareous claystones and siltstones of Badenian age. This sequence is overlain by andesite volcanism products, Sarmatian in age.

– The concentric structure of the Stratovolcano is intruded by younger necks and dikes of diorite porphyrite and andesite intrusions. The Central volcanic zone forms a distinct depression in the wider surroundings of the Zlatá Baňa Village. It is made of a complex of hydrothermally altered andesite rocks. Intense hydrothermally altered are lava flows, intrusions and breccias, in which intruded the diorite porphyrites in the form of necks and dikes. The intrusive bodies have variable forms and dimensions, ranging from isometric stocks (necks) through platy N-S and NW-SE oriented dike bodies. The Central volcanic zone is formed by the extrusions of hypersthene-
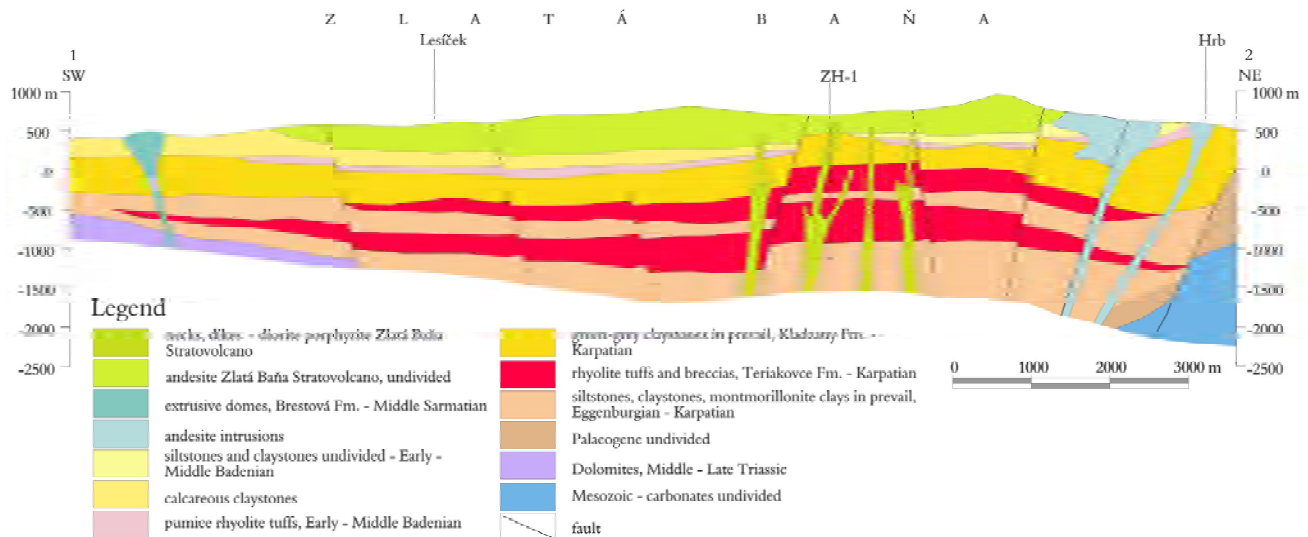
Fig. 4.2.2 Geological cross-section 1-2 Zlatá baňa (modified after Kaličiak et al., 1991)

Fig. 4.2.3 Geological cross-section 3-4 Zlatá baňa (modified after Kaličiak et al., 1991)

biotite andesite, exposed at the surface in the SE segment. The extrusions are morphologically distinctive domes of isometric shape with more than 300 m diameter. The entire complex is disturbed by a system of younger faults of dominantly N-S directions. Relevant data have been retrieved mainly from drilling works (Divinec, et al., 1985, 1989).

– For the purposes of a potential of carbon dioxide storage we consider the following factors:

– The initial stimulus gave relatively high porosity values in volcanic complex in general; both in andesite and in rhyolite products. We have retrieved the porosity values from the data identified by Husák (1986) and Husák et al., (1992). As a rule, the porosity was determined from the boreholes recovery at the site. We have to note that even if the products of andesite volcanism have a higher porosity, for the purposes of this project we have

not accounted for them because of their shallow depth (in relation to the provision of supercritical CO_2 state), as well as virtually no sealing of their superincumbent - they are located on the surface, which excludes them for the given purpose. According to the above author there were found porosities approximately 9% in the rhyolite (115 samples), in rhyodacites 5-9% (125 samples) and in the rhyolite volcanoclastics they were at an interval of 3.93 – 19.7%. In comparison, the clay sediments, forming a seal between the horizons, do not exceed 0.75% porosity value.

– Two older (deeper seated) rhyolite horizons (Karpatian) we have chosen as a suitable environment for potential CO_2 storage (collectors or reservoir rocks with increased porosity parameters). In their favour proves sufficient depth of approximately 750-2,000 m beneath the surface, which provides conditions for the supercriti-

cal CO_2 status as well as the anticipated good sealing caused by lithological filling of the Lower stratovolcanic structure. The geometric factors interpreted in 3-D views suggest a sufficient volume of both bodies (Figure 4.2.4, 4.2.5), which is an essential criterion for the estimation of storage capacity. If we transformed the morphology of the reservoir horizons into hydrocarbon prospection, so we get to a mixed type of trap - tectonic structure, with a gradual "non-structural" wedging out in the distal zone of the Stratovolcano.

The youngest horizon of the rhyolite volcanoclastics - Badenian and Sarmatian rhyolite tuffs and pyroclastics (which has also sufficient geometric parameters), deposited in the predominantly clay environment, is not located in the sufficient depth in order to reach the supercritical CO_2 state and therefore it has not to been considered for the purpose.

In the calculation of the theoretical capacity we have made a conservative estimation. The average porosity was established on 5%, despite the fact that they were not
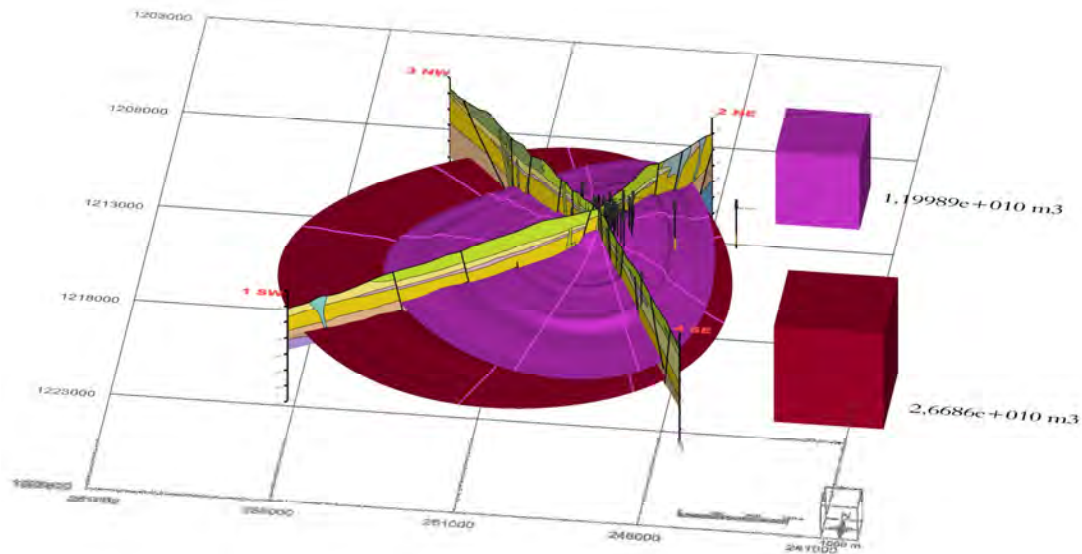
Fig. 4.2.4 Spatial interpretation of rhyolite bodies, view from the South. The cubes indicate the total cubature (Šesták, 2011)
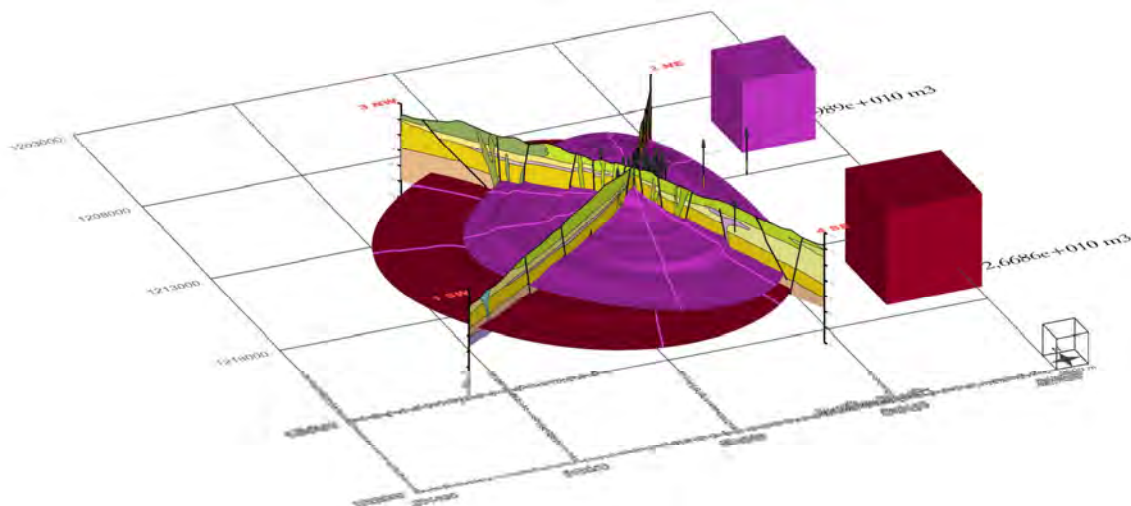
Fig. 4.2.5 Spatial interpretation of rhyolite bodies, SW view. The cubes indicate the total cubature (Šesták, 2011)

rare the porosity values close to 20% either in the rhyolites, or in their volcanoclastics. However, we have kept in mind that the data on the permeability of these rocks are missing, and the high porosity does not secure high permeability. Also for this reason, we have set a minimum value of the sweep coefficient to 2%. When applying the adopted formula we have reached for the top hori-

zon a storage capacity in the volume of 7.8 Mt CO_2 and for the bottom one the storage capacity of 17.3 Mt of CO_2. In summary, this represents approximately 25 Mt, which corresponds to, or it could be close to the parameter for the industrially used deposit. To illustrate the spatial extension of the situation we present a variety of previews on the site in the 3-D view in Figures 4.2.6 and 4.2.7.
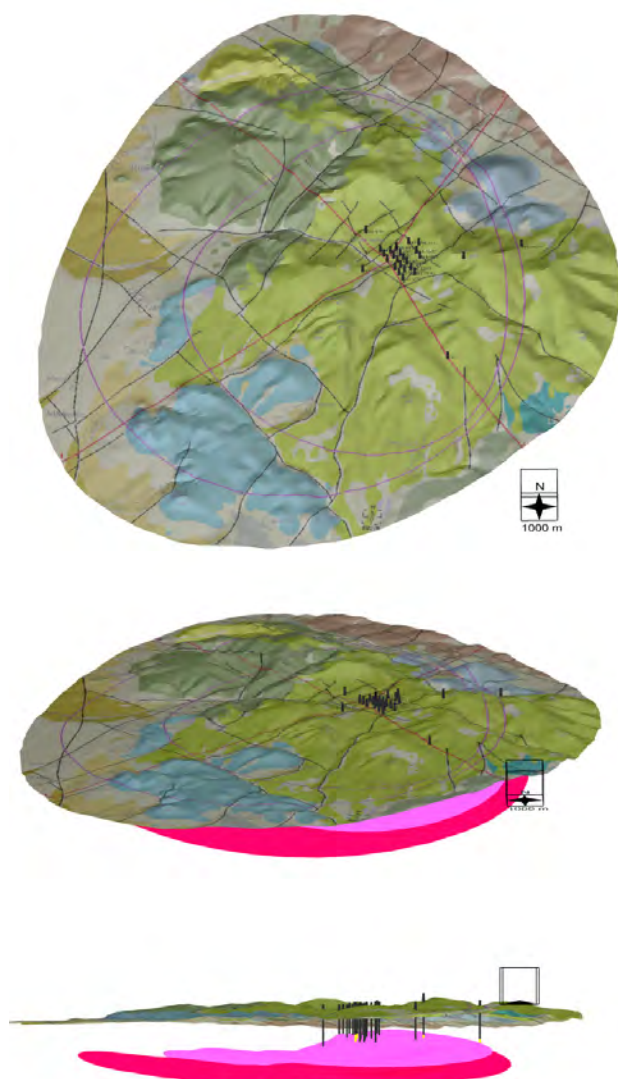
Fig. 4.2.6 3-D view of the rhyolite horizons at different angles (northern orientation (Šesták, 2011)

As a source for the CO_2 storage could be used CO_2 produced by thermal power plant Veľké Kapušany, with an annual production of around 3.5 Mt. The plant is the second largest producer of this gas on the territory of Slovakia. Its distance from the site is about 50-60 km, which is in the context of viable economic criteria, which are currently accepted. On the other hand the calculated storage volumes are likely to be inadequate for effective deposition, because commonly a lifetime of storage is a period of 20-30 years. But it is illusory to think of such a quantity of the injection currently (full year capacity) because usually one injection borehole represents the amount of 1 million tonnes per year. This would then ask for a number of injection wells, or for storage of only a part of the produced gas. But these ideas have already reached too far into the future scenarios that will eventually direct the development of the negative consequences of global warming, the economic situation in the energy market, the overall political climate as well as socio-economic factors.

Problematic (to be discussed) points:

– Although at the site there were drilled 26 deep boreholes (with a depth of 1 km) these are very unevenly distributed for a given task. The construction of the relief of the rhyolite bodies was based on the existing cross-sections (Kaličiak, et al., 1991) and the auxiliary cross-sections (the tossing ones); they served for interpolation using a Microstation code. It is obvious that the shape of the body is definitely "idealized", but basically comes from the general premise of the Stratovolcano setting - a concentric structure.

– Unfortunately, the physical properties of rocks were not studied in detail, so it is not sufficiently verified which horizon has the best porosity parameters. The rhyolite rocks were evaluated in summary, without allocation into lithostratigraphic sequence. In this case, we had to introduce an "expert-assessed" average value.

– There are no sufficient data to determine a justified permeability of the collector horizons.

– The capacity calculation is basically an estimate because it is necessary to introduce a number of coefficients, whereas the aspect of variability, inhomogeneity and anisotropy is virtually impossible to simulate numerically in order to get a plausible result.

– In terms of the security of the potential repository first of all the attention should be paid to the technical condition of the old wells (passable and impassable), which encountered the horizon, and can potentially serve as an escape route from the repository.

– Another potential risk pose young meridional faults, which disturb the structure of the Stratovolcano, especially in the near-surface parts. Their function is not known in terms of tightness, while theoretically the more opened upper sections (unroofing effect) might not represent the factual state in the rhyolite superincumbent, it means in the depths interesting for the project.

– The similar risk may pose numerous dikes and necks of rhyolites and andesites, if these feeders are not completely filled-up with volcanic products. We have in mind the mechanical condition of the walls of the tectonic structures, along which these rocks penetrate through older volcano-sedimentary complex. In most cases they will be reinforced by the thermal fringe, but this assumption must not be valid along the whole length of the feeders.

The site presents a peculiarity in the usual assessments so far for the rock complexes suitable for CO_2 storage. In general, the volcanic products do not represent "appropriate" environment for the carbon dioxide storage. From the point of view of capacity, we are in a very "conservative estimate" for the summary value for both horizons in the volume of approximately 25 Mt.

We summarized the aspects, although only indicatively, which have led us to include this object among the appropriate structures. On the other hand, the attention has to be paid to the outstanding storage issues or the
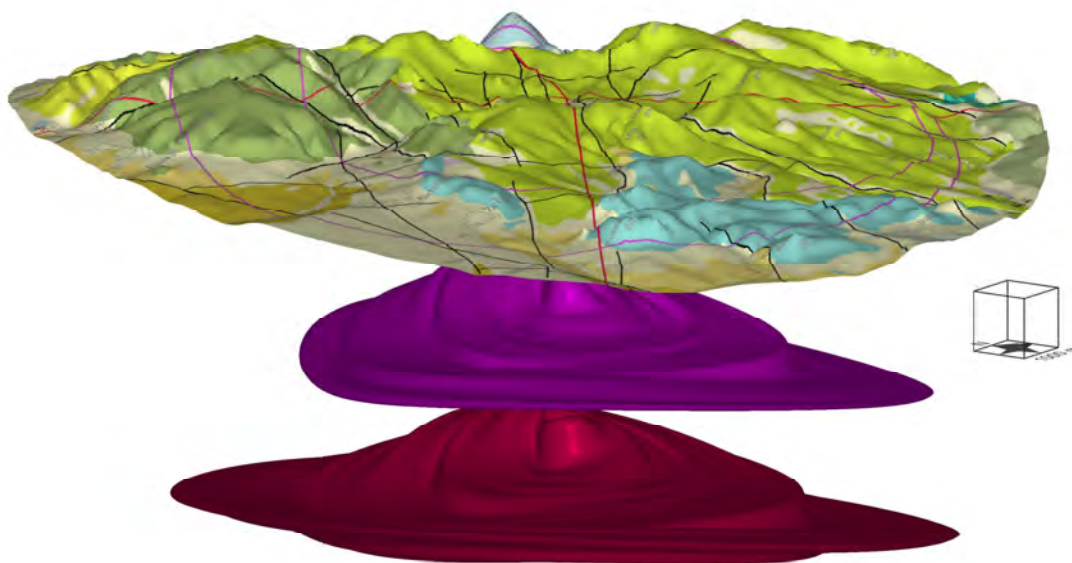
Fig. 4.2.7 Exaggerated 3-D model of the relief and rhyolite bodies (Šesták, 2011)

geological conditions of the site, which will be necessary to verify, because they could affect potential repository. We are still only at the level of theoretical considerations and, therefore, if the current situation should arise to tackle the issue of storage, in the first place is the necessity to verify the practical storage options as soon as possible through a pilot project, the results of which will be crucial for the consideration of the potential repository on an industrial scale.

4.3 Levočské vrchy Mts. and Šarišská vrchovina Upland

In terms of the geomorphological division (Mazúr and Lukniš, 1978) occupies the territory of interest Poprad and Hornád basins, Levočské vrchy Mts., and Šarišská vrchovina Upland and Spišsko-šarišské medzihorie Intermountains. In terms of regional geological division (Vass, et al., 1988) it forms the Popradská and Hornádska kotlina Depressions, Levočské vrchy Mts. and Šariš Palaeogene. The Late Eocene sediments transgraded upon various members of the Fatricum, Hronicum, or Gemericum units. The whole territory was dissected by the younger stages of Alpine Orogene in the series of blocks (normal faults, overthrusts), while in the North and northeastern part the more plastic complexes were folded (Gross et al., 1999). Some faults are morphologically distinctive, and accompanied by springs of ordinary and mineral waters with the formation of foam-stones and travertines. The area was explored for hydrocarbons and geothermal energy resources, with the corresponding great amount of geological works. Their results were verified by deep drilling. Whereas the considerable part of the territory is utilised for balneologic and recreational purposes, our interest was focused mainly in the "classic" Hromoš-Šambron anticlinal zone as the continuation of Lipany elevation structure, which was the main target in

the search for hydrocarbons in the previous century. Therefore, at this stage, we're looking at two sites that could be potentially considered as storage of CO_2: Lipany and Plavnica.

4.3.1 The Lipany Structure

To-date knowledge

The Lipany structure was the subject of prospection for hydrocarbons in the 80ties of the last century, with numerous seismic works, which interpreted in this territory the elevation structure of the basement, which was parallel to the direction of the Klippen Belt. The structure is located in its immediate vicinity (1-4 km).

On the basis of the results of these works (Leško et al., 1974) a deep borehole - Lipany-1 (depth 4,000 m) was drilled in the scope of the project "Research into the deep structures of the Western Carpathians, with regard to the occurrence of oil and gas" (Leško et al., 1983). The borehole was situated relatively close to the Klippen Belt - about 1-1.5 km from its southern edge (Fig. 4.3.1.1). The borehole, inter alia, drilled through a small occurrence of hydrocarbons in the vicinity of the Palaeogene basement; this led to implementation of another 5 deep boreholes (depths of about 3,000 m), in order to determine and verify the hydrocarbon perspective of the site. However, despite these small signs of oil presence, the effort did not produce encouraging results from this point of view.

The Lipany elevation structure is genetically tied to the Mesozoic basement elevation, parallel to the course of the Klippen Belt. In the NW-SE direction it is split by Červeník fault dipping towards SE. In the transverse direction the structure is dislocated by numerous normal faults (Rudinec, et al., 1988). According to the hydrocarbon evaluation the natural gas is found in several hori-

Tab. 4.3.1.1 Overview of the basic parameters of the Lipany boreholes

Well No.	Thickness of Palaeogene (m)	Thickness/depth of horizon (m)/ hydrocarbon indicia	Well depth (m)	The deepest body	Note
Lipany 1	2,790	40/2,360-2,400/yes	4,000	Carbonates T2-3	Productive horizon of gas
Lipany 2	2,870	225/2,455-2,680/yes	3,500	T3	
Lipany 3	3,030	410/2,560-2,970/yes	3,100	T3 dolomite	3x productive hydrocarbon horizons 150 m intercalations included
Lipany 4	?	2,250-2,400	3,000	Shales, sandstones Pg	
Lipany 5	2,957	2,134-2,865	3,003	T 2-3 dolomites	
Lipany 6	?	2,290-2,400	2,850	Sandstones, siltstones Pg	

zons, mainly in (or near) 1,800-2,000 m depths, at the Palaeogene base. In addition, there was a light presence of paraffinic oil. The methane is either with low nitrogen content - up to 1%, or with its share of nearly 50%. The collectors are fine-grained, at places coarse-grained calcareous sandstones, intensely cemented, which show great facies variability. Some collectors are saturated with CO_2 up to 85.3%. The trial tests have shown, that the calcareous component is a favourable factor, because after acidizing (30% HCL) the capacity increased from 10,559 m^3 to 70,000 m^3/24 hours. From the borehole Lipany-4 for the first time in the Eastern Slovakia oil was exploited from the depth of 2,239-2,303 m in a quantity of 20-30 m^3/24 h. The paradox here is that no water-bearing aquifer has been identified within the Palaeogene horizons.

The surges of natural gas have been found in all of the Lipany wells. The main component was methane, an average of 80-90%. According to the operative reserves calculation, the borehole Lipany-1 was quantified as economic reserves in the volume of 25 148 000 m^3 (Rudinec, 1988), in what was then the category C2. Other reserves are considered to be non-economic. The quantity of the horizon in the borehole Lipany-1, after converting the density parameters and application of formation factor, constitutes approximately 600,000 tonnes of carbon dioxide. The calculated amount in terms of the practical use of CCS would be only the volume suitable for a pilot project. In the framework of the project, we conducted a review of the horizon intraformation breccias, which are considered to be an aquifer. The original interpretation by Rudinec (1988), interpreted them as the product of slumps within the submarine channels of the Palaeogene sequence. These horizons, however, have considerably large thickness and extension. On the other hand, the presence of the troughs in such a frequency and thickness in such a small space seems unlikely. We, therefore, on the basis of considerations, as well as on the basis of the data from the other areas of the Inner Carpathian Palaeogene (Plavnica), reinterpreted this factor as a continuous, variably changing layer (Fig. 4.3.1.2). This way we have achieved significant space of water-bearing rocks, potentially suitable for the CO_2 storage. The question of the

eventual use of such a small quantity of gas to supply the vicinity of the site, which could be exploited as a by-product of the CO_2 injection (Enhanced Gas Recovery), remains open, because it could substantially improve the economic parameters of the storage.

In terms of potential CO_2 storage the collector's over-burden is made of Šambron Member, represented by alternating layers of calcareous sandstone and sandy limestone with horizons of non-calcareous claystone. The primary porosity of the calcareous sandstones and sandy limestones is reduced thanks to processes of diagenesis and cementation; the porosity value is less than 2%. These rocks are only slightly jointed, the porosity ranges just in tenths of a percent, and therefore has no practical significance. The permeability of the rock matrix is zero, the permeability of a few cracks is low to moderate - up to 20 $nm^2.10^3$, the joints' width is in the range 0.02-0.04 mm. The collector properties of rocks are rated as inappropriate (Jandová, 1986). In the sections where the coarser facies are developed, the situation is similar - the cementation has filled up the intergranular pores and low permeability have the crevices of very small effective widths. Therefore, this aspect of the Šambron Member confirms its suitability as sealing horizon.

In terms of potential CO_2 storage, the intraformation marly breccias appear to be suitable collector, located close to the Palaeogene complex base; the microfossils content confirmed their Cretaceous and Jurassic age (Rehánek, 1985). These rocks are considered to have more favourable hydrogeological characteristics (Jetel, in Gross, et al. 1999). The author admits that in some parts of the carbonatic breccias it is possible to assume increased permeability of the parameters. Due to the fact that the complex is somewhere very thick - e.g. in the borehole Lipany-5 almost 750 m, the assumption is realistic that certain horizons in terms of the needs of the pilot project would be promising. In particular, the top part of the intraformation breccias at a depth of 2,134-2,157 m could be suitable, where the yield of 11,100 m^3/24 hrs of CO_2 was observed (Rudinec and Řeřicha, 1985), because the quantity equals to approx. 7-9 kt. However, the borehole was liquidated as negative in economic terms (search for hydrocarbons).
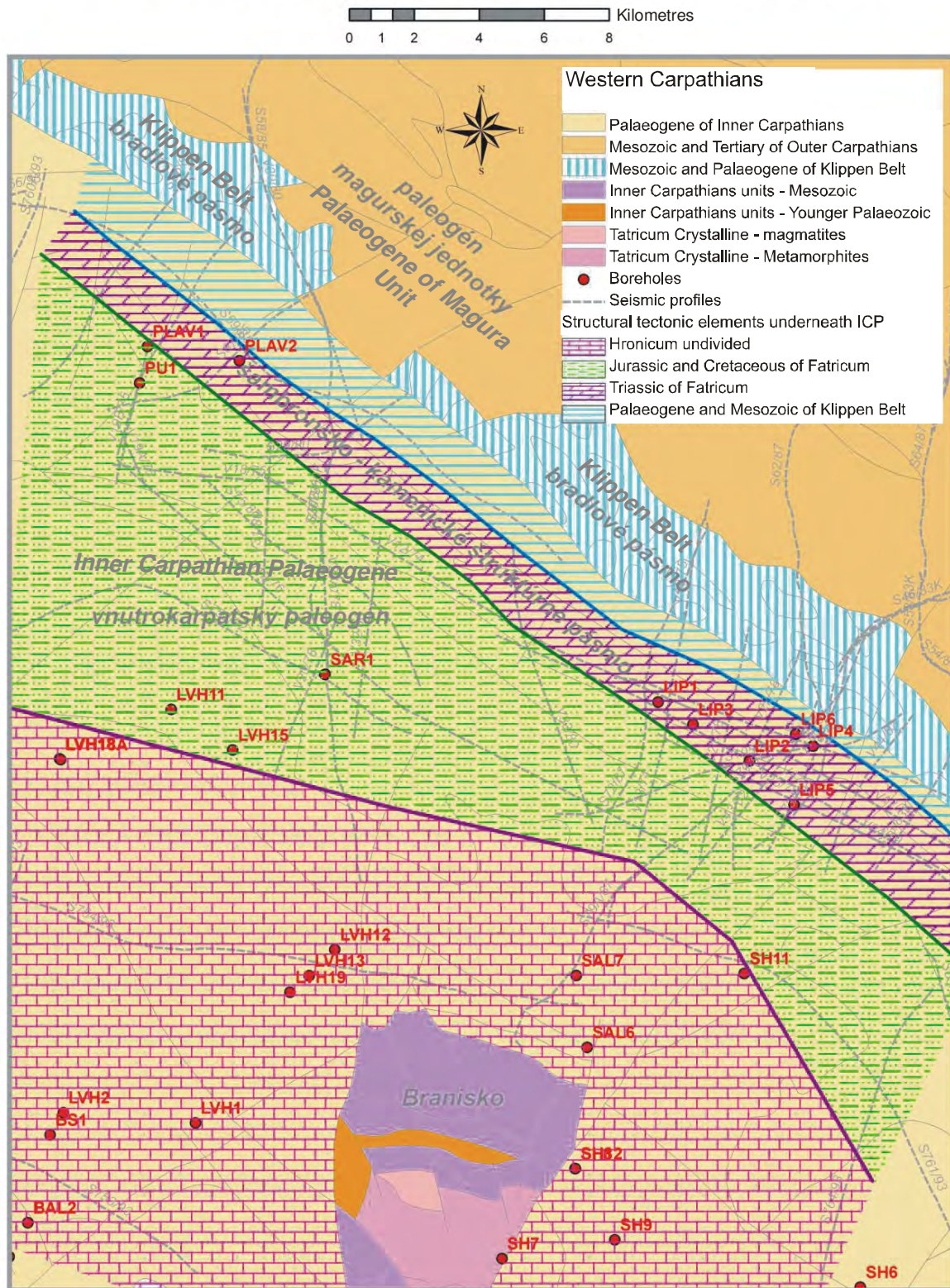
Fig. 4.3.1.1 Structural-tectonic units in the Pre-Tertiary basement of wider vicinity of Lipany (according to Kráľ, et al. 2009)

The complex, which is considered as collector - brecciated limestones and dolomites, lying stratigraphically close to the Palaeogene base, has a relatively good collector properties. The rock is rated as a good collector, with joint porosity from 3 to 5%. Although in this case in the pores reduction cementation played the role, some crevasses remained loose with calcites crystals on cavities' walls. The fissures are fairly abundant, often branched, mutually intersecting, with a width from 0.02 to 0.06 mm which is a space suitable for transition of gaseous and liquid fluids. Total primary porosity, along with the joints one, is around 3%, in areas with small cavities it is
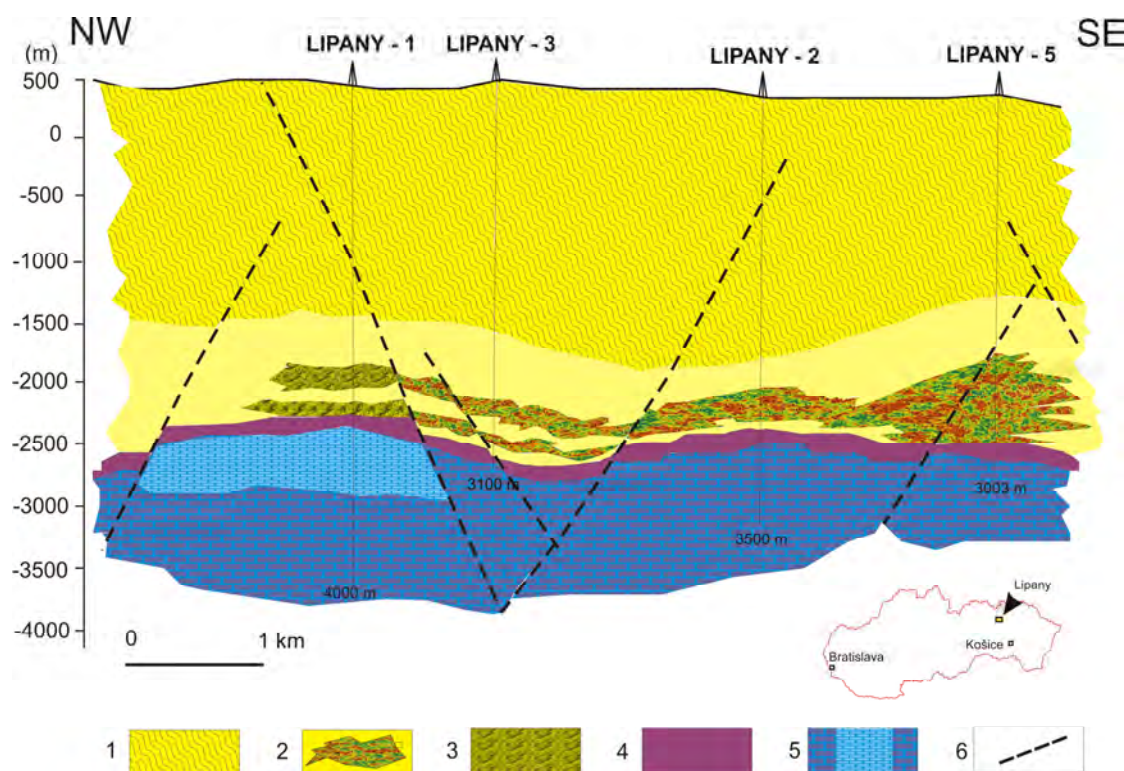
Fig. 4.3.1.2 Geological cross-section through the Lipany elevation axis (modified after Rudinec, et al, 1983)
Explanatory notes: 1-siltstones and claystone in prevail, 2-horizon of intraformation breccias in claystone collector horizon, 3-gas deposit, 4-variegated shales-Keuper, 5-carbonates, collector of geothermal water, 6-faults

around 5%. They are often developed by stylolith sutures. The stylolithisation process, however, does not have a significant impact on the improvement of the collector properties of the rocks. The permeability of the brecciated carbonates is evaluated as good and reaches values of 50-100 nm^2. 10^3.

In the collector's bedrock there is developed an impermeable horizon of Carpathian Keuper - variegated brecciated claystones.

Potential utilisation of the site

The city of Lipany plans to take advantage of the deep thermal borehole Lipany-1 as a source of geothermal water for construction of a water park with associated infrastructure. For this purpose, the project "Lipany - geothermal energy" (Kráľ et al., 2009) was solved. Intake of geothermal water is expected from Pre-Tertiary basement, which was encountered in the exploratory borehole Lipany-1. The objective of the geological project was to verify the source of geothermal water with a temperature of approximately 100 °C, a yield of free overflow up to 10 $l.s^{-1}$ and the total mineralization at the level of 5 $g.l^{-1}$. These data are based on the results of the tester tests carried out during the borehole Lipany-1 drilling.

This objective has been achieved, because the borehole has been made passable and the reserves were calculated, as well as the regime of geothermal waters withdrawal (Kráľ et al., 2009). To ensure this objective there was designed complete technical reconstruction of the

borehole Lipany-1, implementation of sounding measurements in order to allocate water-bearing horizons, intensifying and perforation works, and realisation of a long-term hydrodynamic test for the purpose of determining the exploitable amount of geothermal water from the source, including its liquidation after its utilisation for thermal purposes. Further works consisted of assessment of pressure and temperature in the hydrogeothermal structure in the vicinity of the drill, the calculation of the hydraulic parameters of the geothermal water collector, determination of the gas evasion point, chemical, isotopic, and radiological analyses of geothermal water samples and the accompanying gas, and the determination of the age of the geothermal water.

The problem is the high content of carbon dioxide in the water of the collector horizons of Fatricum, because after trespassing the evasion point there occur a considerable creation of incrustation of carbonates in the inlet tubes and therefore the use of inhibitor is an unconditional necessity. In order to get more instructive idea of the situation we depicted 3-D models of relevant geological structures, displayed in the figures 4.3.1.3 a, b.

In addition to this objective, which is the most realistic and in terms of the acceptance by the population perceived as the most convenient, the following factors underpin the meaning and wider use of the structure.

In view of the high levels of CO_2 in the geothermal water and the existence of a small natural gas deposit within the Palaeogene superincumbent of the Fatricum carbonate reservoir it opens up the possibility of CO_2
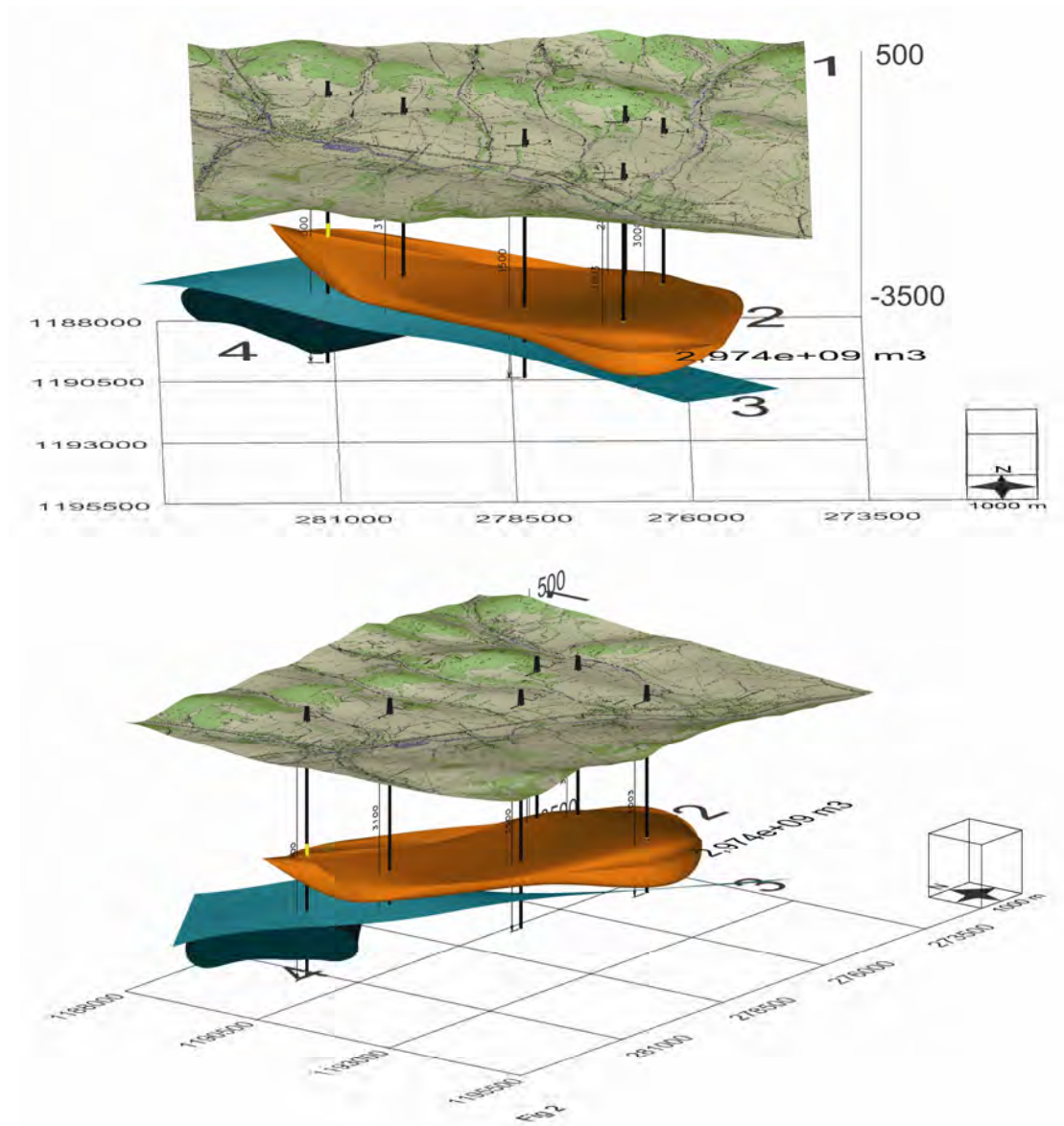
Fig. 4.3.1.3 a (top), b (bottom) 3-D view of Lipany elevation with the essential exploitable geological objects (Šesták, Kucharič & Bodiš, 2011)
Explanatory notes: 1- relief of the surface of the ground, 2-collector horizon - intraformation breccias, 3-Pre-Neogene basement, 4-collector horizon of geothermal water

injecting into the gas deposit, which would alleviate its exploitability and gas thus obtained could be used for the energy needs of the planned water park (ca 1.5 mil. t/ year). It is understandable that such activity would require additional costs (additional borehole with associated infrastructure), but on the other hand, it would be possible to store CO_2, which deflation into the atmosphere would have to be subject to the emission limits. According to preliminary estimated capacity, the volume of methane would satisfy the pilot phase of CO_2 storage. Of course, the population attitude to such a solution would have been significant.

After filling up in the volume of the gas deposit and its extraction it would be possible to proceed to the CO_2 storage within the intraformation breccias, which we have reinterpreted. Thus we have got the volume of the 10 Mt in our capacity estimates, what is already sufficient to

build an industrial-scale CO_2 storage capacity. However, similarly as in the previous case, we would have to count with a strong resistance from the public.

Of course the last two steps, although to-date they look unlikely, they remain as a potential backup for the issue of CO_2 storing. The actual use of such sites will depend on the overall geopolitical situation in the medium term and the development in energy prices, the situation in the field of climate change, as well as in the level of prices of the CO_2 discharge permits. Of course, we can't forget about the attitude of the public, which is in the vast majority of these cases fundamentally negative.

4.3.2 The Plavnica Structure

The structure of Plavnica is located in the "Subtatric Group" of the Inner Carpathian Palaeogene at the southern
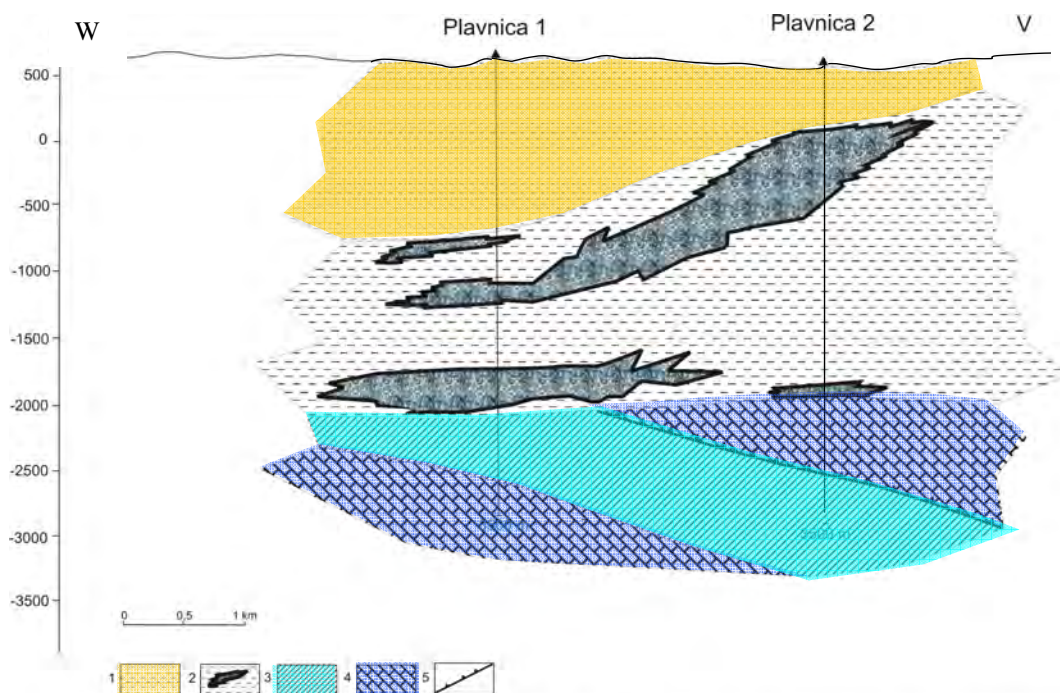
Fig. 4.3.2.1 Geological cross-section through the boreholes Plavnica 1 and Plavnica 2 (modified after Rudinec, et al., 1983)
*1-clay, siltstone, sandstone (Flysch sequence); 2-limestone, dolomite, sandstone, strongly brecciated, intraformation breccia located in clayey environment - **considered as potential storage space;** 3-calcareous-dolomitic clay (Jurassic?); 4-mostly carbonatic complex (Triassic); 5-assumed overthrust plane*

foot of the Klippen Belt. Geographically, it belongs to the north-western part of the Šarišské medzihorie in Ľubotínska pahorkatina Upland (Mazúr and Lukniš, 1980). The structure is situated between the villages of Šambron-Plavnica and Hromoš. In this area the elevation structure was detected by reflective seismic investigation; the structure is assigned to the Hromoš–Šambron elevation zone. In essence, it is a continuation of the Lipany elevation structure of the basement, protruding here from south-east. However, it is very difficult to interpret the seismic image in the internal structure of the Palaeogene and the interface Palaeogene/Fatricum is quite problematic, because of the records are not of sufficient quality.

In the top part of the structure there was implemented Plavnica 1 borehole with a depth of 3,500 m. Another borehole Plavnica 2 was located in the easterly direction in the same structure with the same depth reached. Both wells have drilled-through the Subtatric group and encountered Fatricum. Oil and gas indications in Palaeogene and Fatricum proved to be uneconomic, even though the contents of hydrocarbon gases from the borehole Plavnica 1 from Mesozoic were surprisingly high. The main economic result was a detection of the thermal medium mineralized water (approx. 10 g.l^{-1}) with the temperature at the borehole collar of 45-50 $^{\circ}$C and yield of max. 3.9-4.6 l.s^{-1}.

In terms of CO_2 storage distinctive feature of the lower part of the Palaeogene formation may be interesting - the incidence of a number of horizons of the intraformation conglomerates and breccias. In the borehole Plavnica 1 they are more prominent and more numerous

from the depth of 1,350 m, in the borehole Plavnica 2 they are less pronounced in an interval of 1,700-2,500 m (Rudinec, et al., 1989). Dominant material of conglomerate are pebbles of carbonates (limestone and dolomites). There occur also pebbles of shales, siltstones and quartzose sandstones. The cement has the character of nonassorted polymictic psamite (Řehánek, 1988).

The most distinct intraformation body is in the borehole Plavnica 1 at a depth of 2,306-2,657 m. It is made of medium- to coarse-granular dolomites, which are disrupted by omni-directional crevasses of varying intensity. A significant number of cracks is open. This horizon caused a reflex of seismic rays which was regarded as an elevation structure. Both drillings encountered the Mesozoic carbonates, which are classified as good collector, with the inflows of the mineralized saline thermal water, and carbon dioxide, but with a small amount of hydrocarbon indications.

The horizon in the borehole Plavnica 1 has the original porous space cemented with calcite crystals, so the intergranular porosity porous amounts to only 2%. At a later period the rock was disrupted by crevasses of 0.02-0.06 mm width, enabling a propagation of both gaseous and liquid fluid (Jandová, et al., 1986). The permeability is rated as good - 200 nm^2.10^3. The authors assess the rocks of the Palaeogene base as pore-joint type of collector with a low total porosity, but a **good joint permeability**. The Mesozoic carbonates are rated at the same level, with the difference that the permeability is **moderate**, rarely **good**. Almost similar characteristics are valid for the rocks encountered in the borehole Plavnica 2 (Jandová et al. 1988).

Similar to the site of Lipany, the intraformation bodies were interpreted as a few hundred meters thick lenses, as the product of sedimentation from the submarine channels. For the reasons discussed at the aforementioned Lipany site we reinterpreted their course in similar way, we have got a bulky body, which could serve as a CO_2 repository. Such an idea is documented by geological cross-section (Fig. 4.3.2.1). Total capacity is estimated at approximately 5,000 kt.

The site might be a good place for the implementation of the pilot project. However, the problem may be the technical condition of the two boreholes.

4.4 The Zboj Structure

In the framework of the project Magnetic Map of the Slovak Republic (Kubeš, et al., 2008) a ground-based magnetic method (total vector of the Earth's magnetic field) was applied for measuring the eastern section of the Outer Flysch space. Although the Flysch complexes are typical of magnetic materials absence (Ondra and Hanák, 1989), however in the north easternmost tip of Slovakia, on the border with Poland and Ukraine (fig. 4.4.1), a relatively significant negative anomaly of almost rhomboidal shape was detected with a diameter of about 5 km and amplitude to 100 nT. The anomaly is situated in the area between the municipalities Zboj and Nová Sedlica. In the northwest direction it continues to the village Runina. The territory belongs to the region of Bukovské vrchy Mts. The main ridge of the mountains is of the N-S direction and actually creates the western boundaries of the anomaly. From the morphological point of view, a significant part of the anomaly is located within depression formed by a sudden change in direction of valleys (almost 90°), conditioned probably by fault structures (see Figure 4.4.2). From the geological point of view the territory belongs to the Dukla geological unit. At the surface, there were not detected rocks that could cause this anomaly. Whereas the Flysch sequences are without magnetic rocks, it is obvious that we have captured the effect of a magnetic object, "coming" from the basement of the Flysch complex which had penetrated the Flysch sequence,. Therefore, it had to be younger in age, and its roof did not reach the level of the existing topography, apparently depleted of its kinetic energy (Fig. 4.4.4).

It is an interesting fact that the borehole Zboj-1 (Ďurkovič, et al., 1982), which was situated in the eastern zone in this part of the territory of the Flysch Dukla unit, was set about 6 km to the SW of the anomaly, in the valley of the Zboj Brook, North of the village of Uličské Krivé. Of course, at that time the discussed magnetic anomaly was not detected, because this part of the Slovak territory had not been investigated by the magnetic measurements. In the light of the interpretation of the seismic measurements - two profiles end close to the anomaly - this part of the territory was considered to be an elevation, the Pre-Tertiary bedrock was interpreted in depths of around 2,500 m (Mořkovský,

1992). The borehole drilled-through four complexes (Ďurkovič, 1982), which are presented in the Tab. 4.4.1.

From the hydrogeological point of view the Submenilite Member is rated as an insulator layer, Cisna Member as semi-aquiclude or semi-aquifer, Łupkow Member as aquiclude and Zboj Member as an aquifer. In the borehole there were detected gases surges - methane 92.1-96.3%, particularly in the Łupkow Member in the depths of 2,900-3,663 m. In the Zboj Member in the depths 3,694-3,992.5 and 4,690-4,724 CO_2 surges as well as the saline water inflows were detected.

From the oil-deposit point of view the most perspective was the upper part of the Zboj Member, which was tectonically disintegrated, even with the presence of cavities. Pumping tests were done only in these Zboj strata and according to the chemical composition these waters are classified as highly-mineralized up to brines with the mineralization of 43.95-56.14 g.l^{-1}. According to the carbonate coefficient these waters are of deep circulation, without being affected by shallow groundwaters (Žakovič in Ďurkovič, et al., 1982).

According to the results of a sounding in the borehole Zboj-1 positive effect of secondary jointing is obvious, because on the basis of these measurements the porosity was calculated at an interval of 2,000-3,000 m at the rate of 8.4%, at an interval of 3,000-3,500 at the rate of 4.6% and at an interval of 3,500-4,000 at the rate of 6.6%. In the last km - up to 5,000 m, the porosity reached only 4% (Rudinec, 1989). Here it is clearly seen of what relevance is the younger tectonics to the density parameters. In the majority of the rocks of the Dukla unit in which the well is located, the primary porosity was less than 2%. This fact indicates that the site was tectonically exposed, which has an effect on its further evaluation.

Significant influence on the hydraulic communication within the Palaeogene and Flysch rocks attributed Jetel (2000) to fissured zones, where he defined them as subvertical zones of intense disintegration, with close genetic and spatial relation to the course of the tectonic discontinuities that often predispose the morphological depressions. They run over stratification and dip of the beds independently to greater distances and represent privileged communications of hydraulic movement of groundwater in larger depths to greater distances.

But it may be noted that at the bottom of the Łupkow Member there has been verified a gas-bearing horizon at the depth interval of 2,900-3,663 m with less intensive, but yet six surge spots of flammable gas (methane) at the test capacity of 900 m^3/24 hrs, using 2 mm nozzle (Rudinec in Ďurkovič, et al., 1982).

Interpretation

After analysis of the magnetic field in the area of interest and possible geological variants we come to the conclusion, that the anomalous body is likely neck-shape object tilted to the Northeast. On the basis of the overall concept of the geological structure of the territory and the

necessary physical characteristics to achieve maximum compliance between measured and calculated curves in a magnetic modelling, we came to the conclusion that the anomalous element should be the product of the Neogene andesite volcanism. Such a notion we applied in 2-D modelling of the magnetic field, and we have achieved a very good compliance between the measured and calculated curves of its total vector. As a possible source we assume Neogene diorite porphyry which generally has fairly strong magnetic properties.

Tab. 4.4.1 Simplified geological profile of the borehole Zboj-1 (according to Ďurkovič et al., 1982)

Depth (m)	Rock complex
0-300	**SUB-MENILITE MEMBER** represented by sandy grey and green-grey non-calcareous or weak calcareous clay-stones alternating with mica silts (Palaeocene)
300-800	**CISNA MEMBER** in the development of typical Flysch. The share of sandstones is from 30-80%, the beds are slightly tectonically disturbed. (Palaeocene).
800-3,800	**ŁUPKOW MEMBER** - claystones - sandstone Flysch. The ratio claystones/sandstones is 4:1. The colour of claystones is dark-grey; calcareous share in sandstones is very variable 1.4-35.7%. (Cretaceous-Palaeogene)
3,800-5,002	**ZBOJ MEMBER** has the main lithotype the massive sandstones with homogenous texture (the content of SiO_2 is 53-89%). The top of the beds is tectonically disintegrated (Late Eocene-to Early Oligocene?)
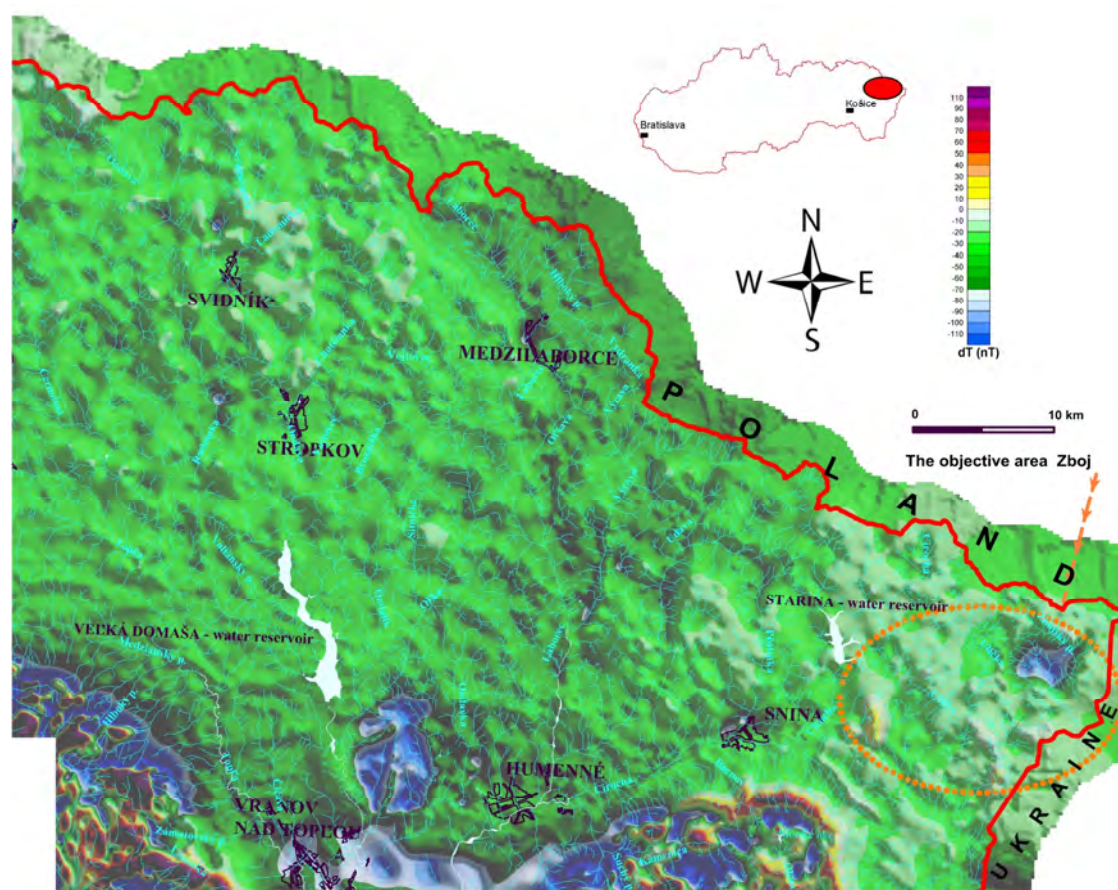
Fig. 4.4.1 Magnetic map of the NE part of Slovakia - Flysch Belt (after Kubeš et al., 2008)

The modelled body along with the geological interpretation is displayed in Figs. 4.4.3 and 4.4.4. The reasons for which we assigned the magnetic anomaly among Neogene volcanism products, we discussed in detail in the work of Kucharič et al. (2013).

Output into CO$_2$ storage issue

For the carbon dioxide storing the premise is important, that in the course of Flysch complex penetration the body of such dimensions affected the sedimentary environment not only thermally but also tectonic deformations occurred in the form of secondary porosity, according to Rudinec (1989) even in the great depths as confirmed by the borehole Zboj-1, which is out of the detected object. Primary porosity is generally very low. We assume that within the exo-contact parts of the interpreted body it should be created an aureole of crushed rocks, surrounding the andesite body, which could be a suitable environment for the storage of carbon dioxide.
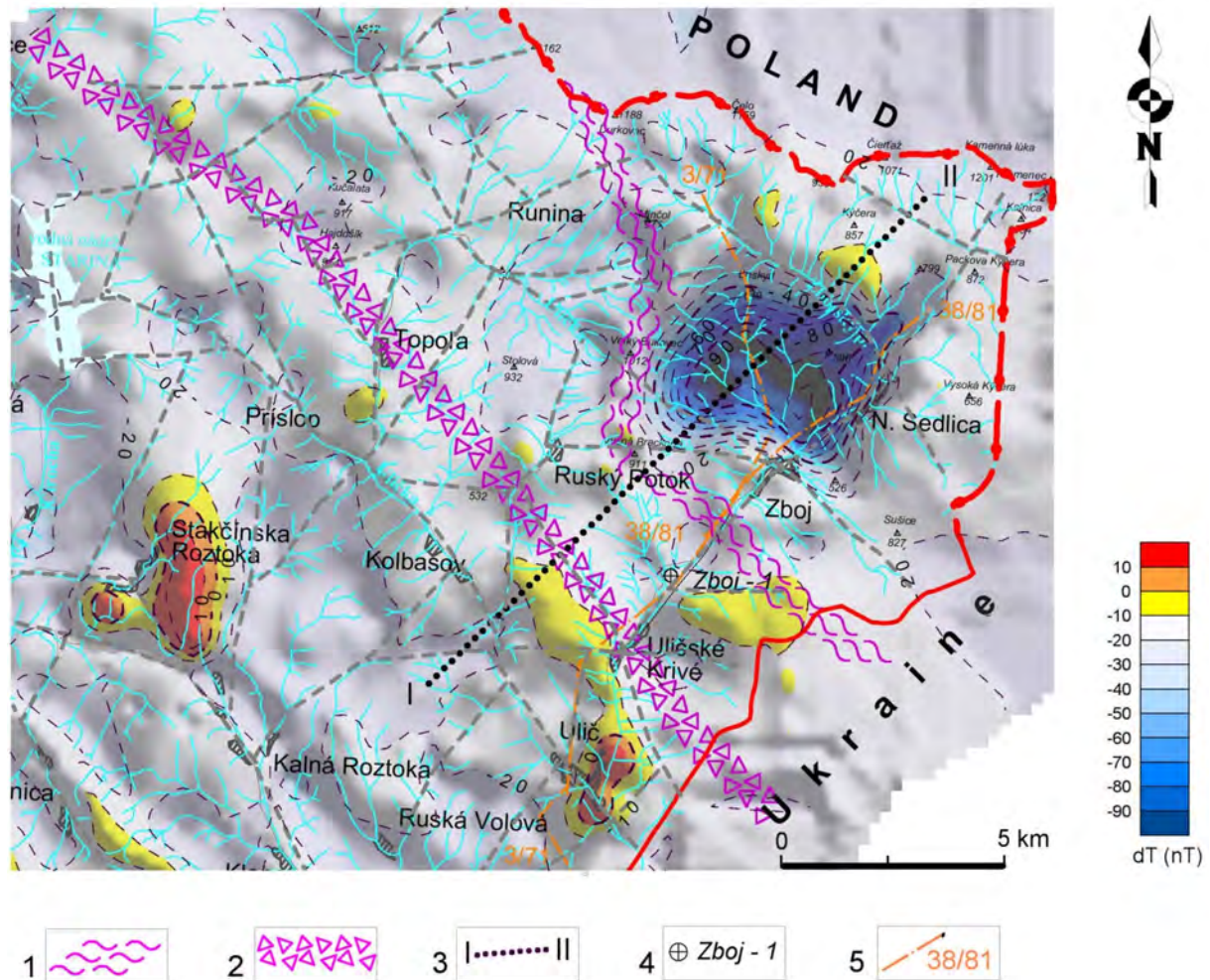
Fig. 4.4.2 Magnetic map of the area showing major Carpathian physical anomalies (gravity low and conductivity anomalies)(after Kucharič et al., 2013). Explanatory notes: 1-the southern boundary of the Carpathian gravity low, 2-Carpathian conductivity anomaly, 3-interpretative profile, 4-location of the borehole, 5-seismic profiles
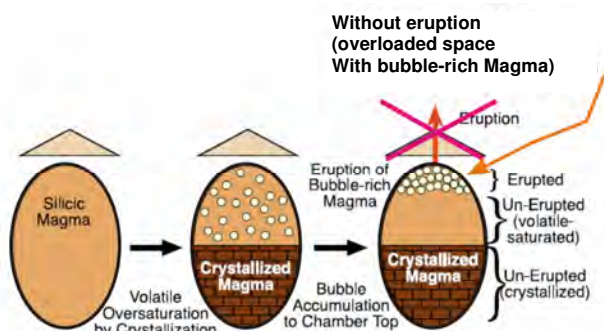
Fig. 4.4.3 Schematic diagrams of bubble accumulation processes in a magma chamber (adopted after Shinohara, 2008)

The effect of secondary porosity we have already mentioned in the previous text.

If we assume subvolcanic body, its lift should be accompanied by the emission of gas, as a result of the separation of magmatic gases from the magma. According to Shinohara (2008) degassing of non-eruptive magma occupies a considerably large space around magmatic body. The expansion of the volcanic gas phase is the main driving force of the magma ascent. In volcanic gases the most common components are water, CO_2 and

SO_2. It is therefore possible that due to the dimensions of the body the gases saturation was limited, the kinetic energy during the saturation was consumed in the course of the ascent, and therefore did not reached the stage of eruptive magma. At the final stop of the magma ascent on the estimated geological border, saturation by the volatile components occurs, which without a doubt increases the porosity of the top of magmatic body. However, we did not include this effect in the calculation of capacity, but with great certainty it represents an added value to the capacity of the storage space. The estimated limit, where the ascent had stopped will be likely a relatively clear cut interface between the sandstones and claystones in the Łupkow Member. Plastic properties of claystone apparently diminish residual kinetic energy, and their almost horizontal roof can represent this interface. This aspect was also modelled in the laboratory conditions, when it was found that each volcanic rock solidifying in a sub-volcanic environment creates a three-dimensional network of bubbles during the drop in pressure, generated by volatile components such as water, carbon dioxide and methane (Berg, et al. 2011). A similar conclusion presents also Sparks (2003), who found out that in more viscous magmas, such as the andesite, or rhyolite ones, the
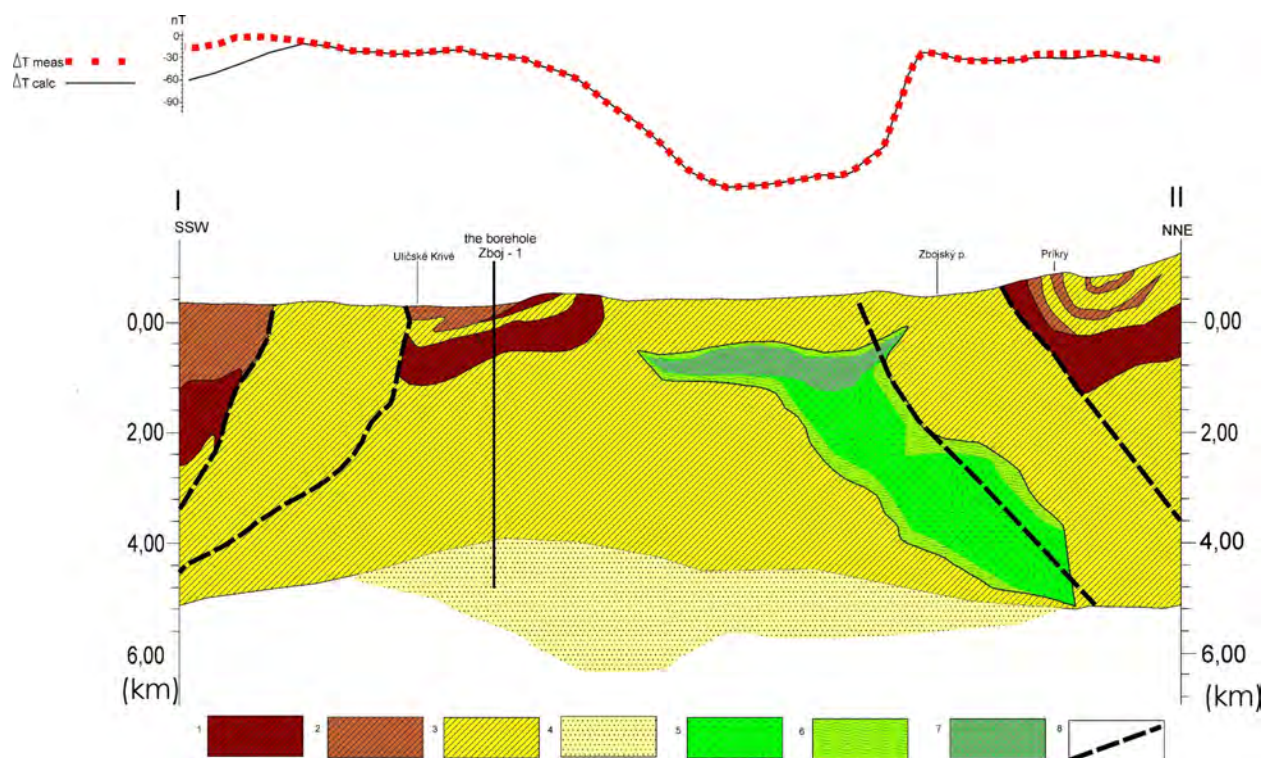
Fig. 4.4.4 The geological interpretation of 2D magnetic modeling (after Kucharič et al., 2013)
1-Sub-Menilite Member, 2-Cisna Member, 3-Łupkow Member, 4-Zboj Member, 5-subvolcanic body, 6-contact zone, 7-oversaturated
zone with volatile components, 8-inferred faults

bubbles of gas rise through a body independently and can create a "magmatic foam" at the top, which becomes so pervious, that the main escape routes do not lead through the contact rock, but along the fault lines.

When calculating storage capacity we were based upon the commonly sed formula for regional aquifers which we modified for a given environment. We approximate the modelled body with the shape of the inclined cylinder. If we assume a crushed aureole around the body, caused by the ascent into the Flysch sequence in the shape of a cylinder with a wider diameter, so for a storage volume we assumed this aureole space, or in other words, the volume of the annulus between the body itself and the intact rocks. The calculation was carried out for different thicknesses of the crushed zone and different depth of carbon dioxide injection, taking into account its supercritical state, thus the depth greater than 800 m below the surface.

We retain a constant carbon dioxide density, porosity, and the coefficient of efficiency. In porosity we were based on data from the borehole Zboj-1 sounding records, albeit with a certain risk that the data may not correspond to the place where the body is located and for the coefficient of efficiency, we used the "pessimistic approach". The result is shown in the database.

Output into the issues of hydrocarbons prospection

Evidence found in the deep borehole Zboj-1 indicates that the site has some of the features of the hydrocarbons potential. The detected and interpreted magnetic anomaly enhances the overall picture of this part of the eastern section of the Flysch Zone. According to the existing information, the occurrence of hydrocarbons in the vicinity of the volcanic rocks is known almost from the hundreds of sites in the world. The volcanic rocks can create hydrocarbon traps because of their good porosity in greater depths. The traps can be created as well between volcanic structures and their sedimentary surroundings. Occurrences of the volcanic rocks turn from these "forgotten areas" to "target ones" in terms of the occurrence of hydrocarbons, as they are the subject of the hydrocarbon prospection. In doing so, hydrocarbons in volcanic rock reservoirs are of biogenic as well as abiogenic origin. The volcanism can effectively increase the maturity, the rate of the generated hydrocarbons, can provide the abiogenic hydrocarbon formation and open their migratory routes (Wang, et al., 2010). Volcanic liquids and gases positively affect the migration of hydrocarbons. On the other hand, although volcanic rocks generally occupy less than a quarter of the volume in the basin fills, the hydrocarbons reserves represent only 1% of the world's proven hydrocarbon stocks. Nevertheless, as a result of the rising consumption of hydrocarbons in the energy sector the volcanic regions are becoming increasingly more interesting objects in the prospection (Liu et al., 2010). In the present case, once again we draw the attention to the previous hydrocarbons presence forecast in the area evaluated (Rudinec, 1989).

Output into metallogenetic issues

Our assumption that the magnetic anomaly is probably caused by the Miocene volcanic andesite body (Trua, et al. 2002), there may be expected in its contact zone mineralization stages, similar to what has been committed in Pieniny andesites in which in the 18th century Au, Ag and Pb were mined (Birkenmajer, et al., 2004):

1st stage - the highest temperature with poikilitic texture of biotite phenocrysts with inclusions of quartz, chlorine apatite and feldspar

2nd stage - lower temperature with the creation of pyrrhotite, pyrite, chalcopyrite, rarely electrum and epidote. This corresponds to the propylitisation phase.

3rd stage - andesite carbonatization, caused by cooling-down of water enriched with CO_2.

4th stage - in which under lower pH and temperature conditions the primary sulphides were replaced by their alteration products, such as: chalcopyrite-covelline, and pyrrhotite- marcasite.

Note: 1st and 2nd stages are accompanied by silicification and argillitisation.

Conclusions

The site is proof that in spite of a generally negative assessment of the Flysch for the purpose, due to the absence of appropriate collector horizons, there may be found in different parts of the Flysch Zone appropriate sites for CO_2 storage, in theory.

In addition, there is a benefit to the fact that, when examining a suitable environment for CO_2 storing, it is often possible to find other interesting facts, encompassing wider geological structures and the practical sphere of use, thereby stimulating a groundswell for the emergence of other potential projects of geological works (Kucharič et al., 2012).

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5. Modelling of geochemical interactions and natural analogues

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Geochemical aspects of CO_2 storage

The geochemical issue of CO_2 storing takes into account the quantitative and qualitative parameters, which can be reviewed on the basis of the existing hydrogeochemical and hydrogeological documentation, experimental verification and the geochemical modelling of the options of carbon dioxide injecting. This approach is the most important tool for simulation of geochemical processes in CO_2-water-rock interactions using mathematical modelling of interactions, as well as natural water in particular hydrogeological structure since its formation. The issue is dealt with for the first time in the conditions of the Western Carpathians, and is subordinated to the existing input options, which have been oriented only to potential aquifers. Isolated or closed hydrogeological structures have been designed to obtain geothermal water or natural healing waters sources.

If CO_2 is injected into the collector which contains brine, it generates transport of substances between the gaseous and the liquid phases. The carbon dioxide dissolves in the brine, while its solubility increases with an increase in pressure and temperature, but decreases with increasing the overall mineralisation of the brine. CO_2 dissolving in the brine increases the density of the mixture. Consequently, the water will evaporate from the liquid phase, thus changing the composition of the gaseous phase. The effect, however, is minimal and is neglected in most studies of CO_2 sequestration into the brine environment.

According to Bielinski (2006) in relation to the CO_2 storage the relevant transport processes in the collectors with the brines may be divided as follows:

1. Advection - the CO_2 movement occurs due to pressure gradient. If the CO_2 is injected into the collector with the brine, it penetrates radially from the point with a higher pressure (at the site of injection) into the areas with reduced pressure within the meaning of Darcy's law.

2. Buoyancy – due to density differences between the gaseous and liquid phases. The carbon dioxide with less density than the brine will ascend into upper parts of the structure and the brine will drop to its lower parts.

3. Diffusion – is caused by concentration gradient. A molecule of CO_2 will migrate from areas of higher pressure to areas of lower pressure until the attainment of steady-state.

The advection is dominant in the injecting period. The buoyancy is a significant transport mechanism, but requires a good vertical communication. The diffusion has a significant effect on the carbon dioxide storage.

A key objective for the injection of the carbon dioxide into the collector with the brine is a guarantee that the injected CO_2 will remain in an underground space during a long time scale. Mechanisms for the CO_2 capture in geological environments are discussed in detail by many authors (e.g. Bielinski, 2006, Ghanbari et al., 2006, Nghiem et al., 2004, Noh et al., 2004, Kumar et al., 2005, etc.). In principle, these mechanisms can be summarized as follows:

1. Hydrodynamic (structural) capture: the injected CO_2 with lower density than the brine will ascend upwards in the form of a cloud until it reaches the impermeable overburden (the barrier will not allow further vertical propagation). Then the carbon dioxide will migrate laterally along the impervious roof.

2. Residual capture (capture in pores, within the intergranular space): at the forefront of migratory cloud the CO_2 displaces the brine and the drainage process is going on. The brine follows the carbon dioxide and fills pore spaces, which had been previously filled with the CO_2 cloud, leading to the capture of CO_2 in the form of a residual phase according to the concept of pore capture (Dullien, 1979).

3. Capture by dissolution: this mechanism is based on the CO_2 capture by its dissolving in the brine. However, it is worth noting that the brine has a lower density prior to being mixed with CO_2, which in turn causes, that the mixture with a higher density will sink and vice versa the brine without CO_2 is going to rise. If the CO_2 will continue to dissolve in the brine, the process will be repeated. This process increases the amount of dissolved carbon dioxide, provided the contact area of the brine and CO_2 is increasing.

4. Mineral capture: CO_2 can react with the mineral phases of the rock environment, which leads to their dissolution and the precipitation in the form of new (secondary) minerals and subsequently to the immobilization of CO_2.

Hydrogeochemical eligibility criteria of hydrogeological structures for CO_2 storing

Geological conditions for the formation of hydrocarbon accumulations in traps are associated also with the issues of migration of fluids in the course of geological-tectonic evolution. Significant tectonic activity of the territory gives rise to a wide range of traps of synsedimentary and postsedimentary origin. The traps of non-anticline type dominate; their generation is not controlled by the anticlinal shape of the layers forming the collector, but by different lithological or geomorphologic factors (Freund, 2006).

Hydrogeochemical criteria for the assessment of the suitability of the hydrogeological structures must be based on clear hydrogeothermal characterisation of the closure of these structures. It is due to the fact that carbon dioxide storing is practically possible only in the geological traps (closed structures), in order to avoid the possibility of leakage to a minimum. On the other hand, it is true that the criteria that characterize the groundwater are not completely sufficient, because the gas and its transport in the rock environment show different migration properties. Therefore, more hydrogeochemical criteria were used, among them the composition of the gases. As screening criteria the following characteristics were selected:

1. The use of Palmer classification modified by Gazda (Gazda, 1971), provided the waters should be of a strong $S_1(Cl)$ type with a characteristic representation of $S_2(Cl)$ component and low or zero content of A_1 and A_2. It should be noted that the greater presence of A_1 component indicates degradation of the original (initial) marine waters, most commonly in the geological past. Infiltration degradation, however, can take place under certain conditions, even in the present.

2. The value of total mineralisation of the water in combination with the $S_1(Cl)$ component. It reflects the value of the palaeosalinity of the waters. In compare to the initial oceanic water it is changed mainly due to interactions in the system water-rock-gas. The average oceanic water keeps in the long run a mean salinity of 35 g.l^{-1}. Generally speaking, if the value of the total mineralization of the water is around the above value, we may assume that the hydrogeological structure is closed.

3. Hydrogeochemical coefficients:

a. HCO_3/Cl indicates the hydrogeochemical closeness or the openness of the hydrogeological structures. Values around 0.1 in terms of CO_2 injecting are already interesting. Typical values are less than 0.1.

b. Cl/Br - genetic ratio, in sedimentary basins with an abundance of brine and hydrocarbons characteristic values are around 500.

c. Mg/Ca – enrichment on Mg represents dolomitisation increase with consequent increase in effective porosity. As an auxiliary criterion, it can be assumed that the ratio expressed in the equivalent is more than 0.8.

4. The content of biogenic elements of iodine and bromine, typical elements that accompany the presence of brine and hydrocarbons in waters thanks to similar conditions of their genesis.

5. The content of gases

Characteristic is the content of non-acid gases. In general, with an increasing degree of closure of natural waters structures (collectors) the composition of the non-acid gases turns from the nitrogen gas with a high content of oxygen to the nitrogen without oxygen with an increased share of methane and, in the deeper parts of the sedimentary basins under conditions of limited water exchange dominates methane type of non-acid gases. They represent biochemical gases, lesser the gas of the chemical origin.

6. The contents of the stable oxygen isotopes. If the isotopic composition of natural waters is lower than the meteoric line with a trend toward the SMOW it suggests a closed structure.

To the above hydrogeochemical criteria it should be noted that confirmation by the other methods and knowledge is needed in order to get the real picture about the possibility of CO_2 injecting in the given region. Hydrogeochemical tightness may not be identical with the hydrogeological one and must be evaluated individually for each structure, or aquifer.

In addition to the hydrogeochemical criteria, we may note the other ones (tab. 5.1), which are very significant in terms of the carbon dioxide storage. These criteria can be termed as the geological indicators and are extremely important both in terms of the reservoir, as well as its roof.

From the hydrogeochemical analysis of groundwaters of the Western Carpathians it follows, that the most suitable collectors, which meet the specified criteria for carbon dioxide storing would have been hydrogeochemical collectors with highly mineralised geothermal waters, then relict marine waters, metamorphosed in the rock-water system only. To store CO_2 absolutely inappropriate are geothermal waters with a petrogenetic mineralisation. However, it is important to note that the brines have increased I and Br contents, which makes them suitable for curative purposes. In choosing the appropriate structures for the storage of carbon dioxide the socio-economic interests are of primary importance, which is valid to-date, and, in particular in the future.

At present, when dealing with the CO_2 storage across the world, a wide range of programmes is used (e.g. PHREEQC, COORES, TOUGHREACT, SCALE2000, etc.); their application in a given geological environment depends mainly on the specific conditions (clay environment, hydrocarbons reservoirs, shales, basalts, etc.) and in a way of their binding to the environment (physical, or geochemical), the specific objectives of the modelling (CO_2 reactivity, multiphase transport in reservoir, design and the geochemical quantification of carbon capture), or the availability and modelling code price.

The first, very important component was the analysis of the issue and the search work. Because the regional research aimed into the geologic CO_2 storage has not been realized yet, it was necessary to analyze in detail the methodology and, in particular, approach in terms of geochemistry and hydrogeochemistry and to adopt them from the world literature. In the world such research began almost fifteen years ago, when it rocketed up with the challenge of the protection against global climate

Tab. 5.1 Geological indicators of CO_2 injection into for the reservoir in the rock environment

	Positive indicators	Warning indicators
Total storage capacity	estimated capacity far greater than the total quantity of CO_2 produced from the source	estimated capacity approximately the same as the total amount of CO_2 produced from the source
Reservoir properties		
Depth	>1,000 m <2,500 m	<800 m >2,500 m
Thickness	>50 m	<20 m
Porosity	>20%	<10%
Permeability	>300 mD	<10-100 mD
Salinity	>100 g.l^{-1}	<30 g.l^{-1}
Overburden properties		
Horizontal connectivity	without faults	horizontal inhomogeneity, tectonic failures
Thickness	>100 m	<20 m
Input capillary pressure	input capillary pressure is much higher than the buoyant force of the estimated amount of the CO_2 column	input capillary pressure is similar to the estimated buoyant force of a rising column of CO_2

Note: according to CO$_2$STORE_BPM_final

change, where CO_2 plays an important role, in conjunction with its negative industrial production.

The up-to-now geochemical and especially hydrogeochemical research in Slovakia was aimed in particular at clarifying the genesis of mineral and geothermal waters (particularly deep hydrogeological and hydrogeothermal structures are a matter of concern for the injection of CO_2). Similarly, the thermodynamic modelling of water-rock interaction – focused on the gas, but not in the sense of entering a high amount of CO_2 in the gaseous and supercritical state into the equilibrium reactions. In other words, the target of interest was groundwater search, defining its origin and quality properties and securing its protection. In the context of modelling the subject of interest has been focused not only in the equilibrium thermodynamic modelling, but also in the reaction kinetics as well as in the reaction transport model.

The most important part was to select and work with the most appropriate geochemical programme, which would offer simulation of various scenarios for CO_2 injecting. The thorough search work identified PHREEQC programme (Parkhurst-Appelo, 1999) as appropriate from the professional and financial point of view. The programme is one of the most used geochemical programmes in the world, which is available for free on the USGS website. In fact, all the previously implemented projects of CO_2 sequestration in their initial phases benefited from this programme. Definitely another important selection criterion was the nature of the input data, which is currently still inadequate as well from the perspective of PHREEQC (such as a modal analyses, the parameters of porosity, etc.). The Programme allows for the characterization of water, in-series modelling of reactions, kinetic reaction, modelling the transport and inverse modelling. There was used the programme PHREEQC Version 2, updated by February 5, 2008. Originally the programme was focused in the modelling of geochemical processes in groundwater at low temperatures and pressures. The problem was a database of thermodynamic constants and mineral phases, which is currently solved by optional database. The Programme contains a databases phreeqc, phreeqd, minteq, iso, minteq4f, wateq4f, pitzer and llnl, which are possible to apply according to the required issue solution. In particular, the pitzer database is very convenient for the application of the equilibrium constants for CO_2 injection, because it has equilibrium constants depending upon high temperature and high ionic strength of the solution and the database llnl, which works with the largest number of mineral phases. Therefore, it can be used also for other modelling of ex situ sequestration – simulation of reactions in the experiments, in particular, with olivine, serpentinite and wollastonite.

The theoretical foundation of the PHREEQC code are known from a number of publications, of which essential are, in particular, Parkhurst-Appelo (1999), Appelo-Postma (1993) and Merkel et al. (2005) and the basic manual, which can be downloaded from the USGS Web site.

5.1 Structure Marcelová

Hydrogeothermal structure Marcelová is located in the south-western part of the Danube Basin (Figs. 4.1.2.11, page 49). The aquifers in the GTM-1 borehole occur in the depth range 795-1,195 m – they are limestone beds, which alternate with red clayey and calcareous shales. At a depth of about 1,195 – 1,450 m red fine-grained laminated and mica-rich sandstones alternate with red, less green-grey shales. Up to the final depth of 1,763.5 m grey to black shaly and thin-bedded limestones and clayey shales predominate. At places thin horizons of clayey shales and fine-grained laminated sandstones are present (Biely, Kullmanová, 1992). With regard to the above lithology, the brine inflow into the borehole sediment is most likely from a fault zone, which conducts the brine from the jointed Early Triassic sediments (Franko et al., 2011).

The brine from the borehole GTM-1 has a value of total mineralization of 126 g.l^{-1} and is of a distinctive sodium-chloride type. This brine was applied in scenario of carbon dioxide injecting. An overview of the status of the mineral phases before and after the injection of CO_2 documents tab. 5.1.1. The modelling detected the biggest changes at given pH and current mineral phases saturation and, naturally, at increase in the amount of total dissolved carbon dioxide in the brine. The phases were selected, which exhibit in the natural state the over-saturation, or equilibrium with brine. The scenario was carried out with CO_2 at an injecting pressure of 3.04 MPa, which at the same time was also partial pressure of CO_2 with CO_2 fugacity of 0.30 at 10 MPa pressure of atmospheric carbon dioxide, which was the subject of modelling.

Tab. 5.1.1 The status of mineral phases before and after the CO_2 injecting

Phase	SI (-CO_2)	Dissolved CO_2	SI (+CO_2)	Dissolved CO_2
temperature	**54**		**54**	
pH	*6.6*		*3.49*	
p CO_2	*0.002 MPa*	*0.0022 mol.kg^{-1}*	*3.04 MPa*	*0.39 mol.kg^{-1}*
andradite	7.77		-18.51	
aragonite	0.3		-2.7	
calcite	0.44		-2.55	
dolomite	1.83		-4.16	
Fe(OH)$_3$	1.63		-2.21	
FeOOH	6.41		2,57	
magnesite	-0.08		-3.07	
quartz	0.01		0.02	
strontianite	0.41		-2.59	
talc	0.98		-17.63	

As regards the content of dissolved carbon dioxide, this has increased after the injection on about 177 times, from 0.0022 mol.kg^{-1} in natural brine to 0.39 mol.kg^{-1}. In view of the mass this represents 17.2 g.l^{-1} of total dissolved CO_2 in the brine after injection. The quantity of CO_2 causes an abrupt change in the pH value on nearly half - from 6.6 to 3.5 and brine solution shall become strongly acidic. Important will be also the subsequent solution reactivity, which will act on the surrounding rock environment. It is clear from the Table 5.1.1 that virtually all phases of the system are not likely to precipitate in their natural state, but on the contrary, they will dissolve, with the only exception of ferric hydroxide. The phase status of quartz will remain unchanged even after the injection of carbon dioxide; it will stay in equilibrium state with the solution. The model is made for a stationary state, the kinetics of the reactions is not included, and it means, the velocity and the time in which they will take place. One fact is obvious, however, that carbon dioxide will dissolve almost immediately in the brine and will generate changes that require evaluation, using the reaction kinetic transport model.

The used programme PHREEQC is adjusted to one dimensional modelling of transport processes, which includes: 1. diffusion, 2. advection, 3. advection and dispersivity, 4. advection and dispersivity in the stagnant zone. The important thing is that all of these processes may be combined with thermodynamic equilibrium states and kinetics of chemical reactions.

At the site Marcelová the transport model was simulated with advection and dispersivity. Partial pressure at the injection was considered for 7.38 MPa and diffusion coefficient was 4.5 . 10^{-11} m^2.s^{-1}.

The results of the modelling of transport document changes in pH during CO_2 transport. The Figure 5.1.2 presents the result of the simulation after 10 years of injection. Brines are considered in the case of carbon equilibrium with calcite and dolomite. Therefore, a change in pH is biased to a certain distance from the borehole, where equilibrium will be achieved after 10 years with the considered mineral phases.
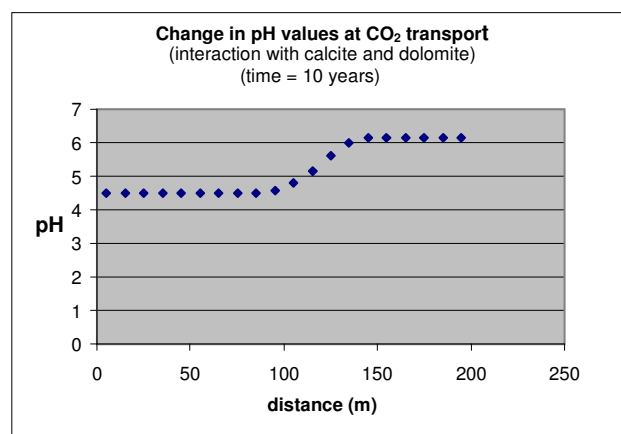
Fig. 5.1.2 Modelled changes in pH transport model

From the chart we can see that the pH value is gradually increased in the range from 100 m to 150 m and then remains steady at around 6.1. This means that at the beginning due to the dissolution of CO_2 the pH is sharply reduced, but at the same time mineral phases of calcite and dolomite present in the solution interact and are being dissolved. The brine in the distance of approximately

100 m away from the CO_2 injection sites no longer loses the neutralisation capacity and the pH value gradually grows, calcite and dolomite stop being dissolved and the system gets into a state of equilibrium. This case occurs at a distance of approximately 150 m from the site of CO_2 injection.

In Figure 5.1.3 the course in total dissolved carbon dioxide content in the brine is shown, depending on the distance of injection for 10 years. Input conditions are the same as in the previous case. It turns out that in the distance of around 75 m from the injection spot the amount of dissolved CO_2 is practically the same, approximately at the level of 0.83 mol.kg^{-1}. Then around the distance of 100 m it drops rapidly to a value of 0.2 mol.kg^{-1}. At a distance of 150 m is the amount of CO_2 close to zero value. This course corresponds very well with the state of calcite and dolomite saturation condition, since, as already aforementioned, at this distance both mineral phases are in equilibrium with the brine.
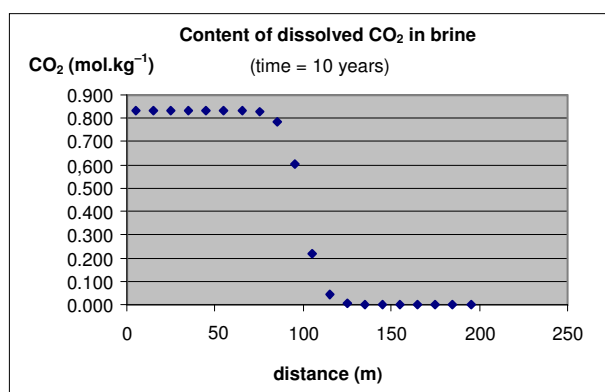
Fig. 5.1.3 Model solution of CO_2 content during transport

The difference between the amount of CO_2 that is captured using the so-called capture by dissolution and mineral capture is presented in Fig. 5.1.4.
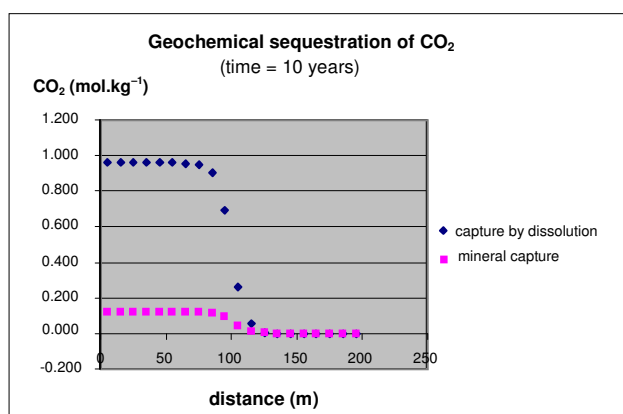
Fig. 5.1.4 Course of CO_2 capture by dissolution in the brine and by mineral capture.

The capture by dissolution is actually identical to the already described total dissolved carbon dioxide content. The mineral capture represents the amount of CO_2 consumed to dissolve calcite and dolomite from the rock environment. Its value is generally much lower in com-

parison with its dissolution in the brine. It should be noted, that the kinetics of reactions was not taken into account, only transport and diffusion.

The situation after 20 years of injection is simulated in Figures 5.1.5 and 5.1.6. Compared with the previous situation, the low pH values will persist within the environment at a greater distance from the site of injection and, of course, the total content of dissolved CO_2.
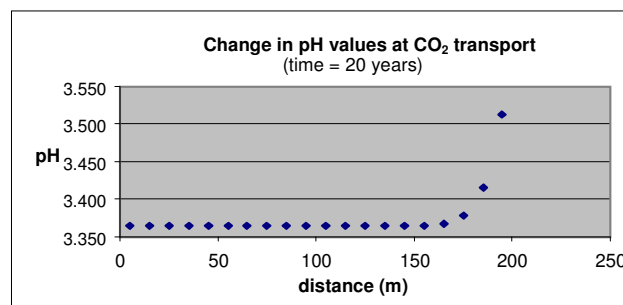
Fig. 5.1.5 Course of the Ph changes after 20 years
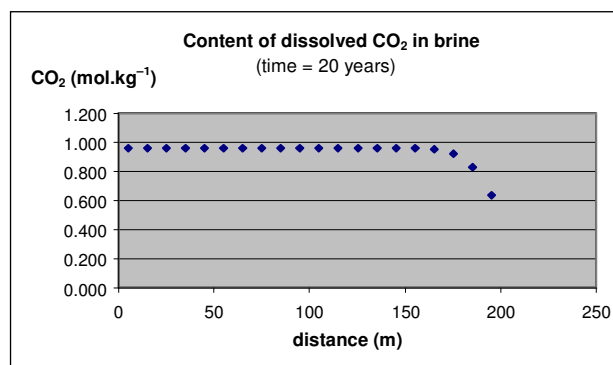
Fig. 5.1.6 Course of CO_2 content after 20 years
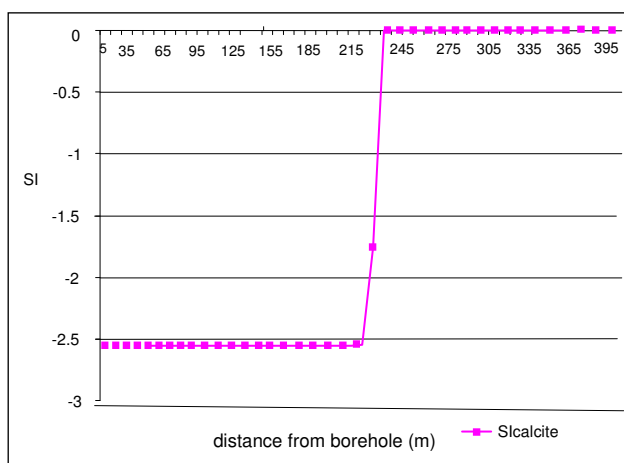
Fig. 5.1.7 CO_2 transport with respect to the dissolution kinetics of calcite.

In the next scenario in the transport model the kinetic module for calcite was inserted. The result of the simulation is documented in Figure 5.1.7. It is obvious that at a distance of 250 m from the point of injection the calcite will be undersaturated when compared with the brine and will dissolve. After then, the calcite will be in equilibrium with brine reaching a steady-state.

5.2 The Láb Structure

Under the term Láb structure we understand the Láb-Malacky Elevation with adjoining sunken blocks. In this structure within the Mesozoic basement there have been uncovered brines with the values of total mineralization from 109.8 to 129.8 g.l^{-1}. They are of distinct Na-Cl type with minimum value of A_2 components, which indicates the closeness of the structure in which they are located. The levels of sulphates in the brines are relatively low, but do not exceed the value of 600 mg.l^{-1} in spite of the presence of anhydrite in collector rocks.

Based on the palaeoreconstruction of the brine in this area, we can say that the Triassic carbonates were overlain by Late Karpatian clays and sands. From this fact it follows that, until the Karpatian period, the whole area was exposed. During the Late Karpatian the whole area of the Slovak part of the Vienna Basin was flooded by the sea, protruding to the Láb-Malacky area, creating lagoons. Within the lagoons due to evaporation brines were formed, which had infiltrated into the Triassic carbonates and were later sealed by Late Karpatian clays. The evaporation didn't reach up to the level of halite precipitation, because the lagoons had been replenished by meteoric waters originating from precipitation and surface flows. These assumptions also supports the value of ^{18}O = -2.4 ‰ in the brine in the depth range of 1,877-2,873 m in the borehole Láb-120 (Pačes, 1983).

The simulation of CO_2 injecting was under the same conditions as in the structure of Marcelová.

The simulation process of injecting took place under the temperature 122.5 °C and the initial pH of the brine 6.4 (Table 5.2.1).

Tab. 5.2.1 Injection and transport conditions

Site	pressure CO_2 (MPa)	temper.	diff. coeff. ($m^2.s^{-1}$)	distance (m)	time (years)
Marcelová	7.38	54	$4.5.10^{-11}$	200	10, 20
Láb-92	7.38	122.5	$4.5.10^{-11}$	200	10, 20
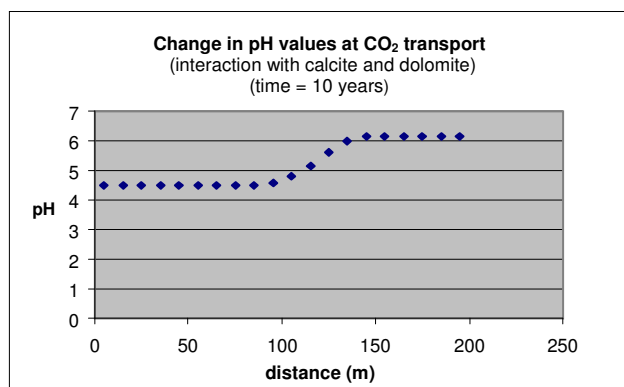
Fig. 5.2.1 Course of pH values at CO_2 transport

From the Fig. 5.2.1 it is evident that at the site of CO_2 injection the pH value drops sharply to 4.49. The change occurs at a distance of up to around 115 m, but its course is not as sharp and, in particular, the pH value is just closing the original one.

A different course is to follow at the CO_2 transport without interactions with rock environment (Fig. 5.2.2). Of course, H$^+$ ions are not being consumed and the pH value is steady at a level of to 4.3 up to a distance of around 155 m. There occurs only the CO_2 dispersion by diffusion and to a distance of 200 m from the site of injection, for a period of 20 years, the pH would rise to a value of 4.5 only.
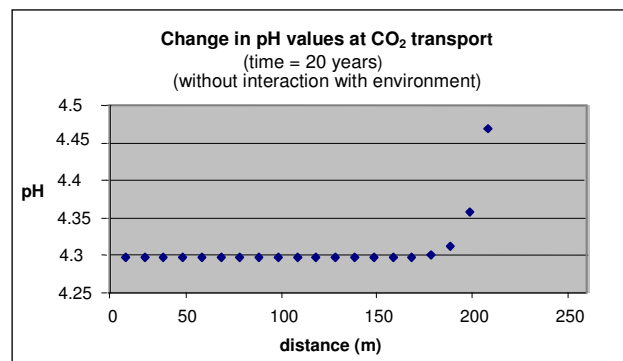
Fig. 5.2.2 Course of pH values at CO_2 transport

The ratio between the capture by dissolution and mineral capture of CO_2 for a period of 10 years of injection shows the Fig. 5.2.3.
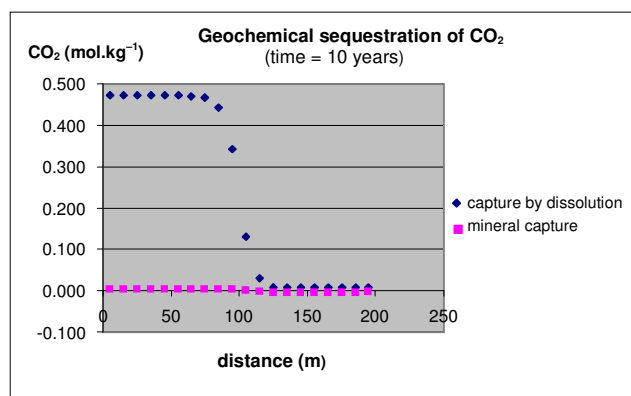
Fig. 5.2.3 Course of mineral capture of CO_2 and dissolution in the brine

The difference between the two types of capture is evident (Figure 5.2.4), the nature of the mineral capture has a much smaller effect and much slower progress.
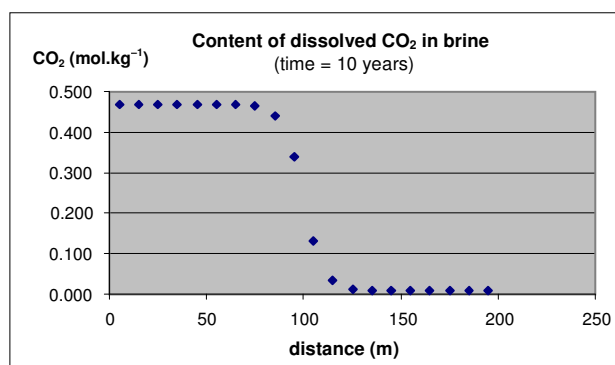
Fig. 5.2.4 Course of dissolved CO_2 content

It is clear that the capture by dissolution corresponds to the already described course of the pH value during the transport in the simulation of steady-state. It is important to note that the calculated CO_2 levels will be distorted by the fact that the modelling was done using the equation for an ideal gas. However, the CO_2 in supercritical condition and the given geological structure does not behave as an ideal gas, this means that its fugacity is not equal to the saturation pressure chart. This fact corresponds also to the amount of dissolved CO_2 in the brine in the Fig. 5.2.4.

5.3 Nature analogues

The study of natural analogues is an important part of the research in options for carbon dioxide storage into the ground. Under the natural analogue we understand a natural accumulation of CO_2 in the geological environment in the form of so-called dry CO_2, or within the groundwater collectors. It is possible to use natural ana-logues to study the properties of carbon dioxide and the conditions (in particular, pressure and temperature), under which its accumulations are formed underneath the Earth's surface. Furthermore, it is possible to track its interaction with the geological environment, as well as impermeable strata that make up the boundary conditions for an accumulation. Similarly, it is possible to study the interaction of water-gas and water-gas-rock, as well. The basis is the fact that similar conditions are hardly to imitate in the experimental laboratory.

In the scope of the project the thematic unit was studied in the context of the carbon dioxide behaviour under the conditions of higher temperatures and pressures. The geothermal water properties from a borehole Lipany-1, as the natural analogue of geothermal water collector with a high content of carbon dioxide were evaluated on the basis of chemical analyses taken during hydrodynamic tests on the collar of the borehole. All the data have been retrieved from the work of Kráľ et al. (2010).

At the exploitation of 10 l.s^{-1} of geothermal water from the borehole the pressure on the collar will be in the range 2.75-2.70 MPa. In the phase ratio of the geothermal water and separated gas under the atmospheric conditions equal to 25 Nm^3.m^{-3} the amount of pure carbon dioxide for 1 hour will be 900 Nm^3; for 24 hours, this is a production of 21,600 Nm^3 of gas.

The modelling (PHREEQC) simulated the quality balance of likely mineral phases in the borehole collar in the water with separated gas and without separated gas. As the likely mineral phases (phases, which will form of the water) are the ones whose index of saturation under the given conditions is greater than 0, or 0.2.

In the case of gaseous phase separation, in the condition of partial CO_2 pressure 0.0443 MPa and temperature 91°C, the geothermal water is strongly oversaturated with mineral phases as indicated in the Table 5.3.1 and virtually all the CO_2 is dissolved in the water (SI = -0.36). These can be summed up in two geochemical categories. The first one is the oversaturation with respect to all potential mineral phases of carbonate equilibrium and the second one is the oversaturation in respect to all mineral

phases with trivalent iron. In the first case the result of the simulation is the formation of carbonate incrusts and in the second case the creation of mineral phases on the basis of trivalent iron, which gives the water a typical brownish yellow haze. At the same time, we can observe an increase in the pH of the water, which is caused by the lack of carbon dioxide in the system, because it was separated away.

Tab. 5.3.1 Likely mineral phases of the geothermal water under the conditions at the borehole collar.

Min. phase	SI (with gas separated)	SI (without separation)
CO_2	-0.36	1.30
p CO_2 (MPa)	0.0443	2.022
aragonite	2.13	0.58
calcite	2.27	0.72
dolomite	5.14	1.98
dolomite-ordered	5.15	1.99
dolomite- disordered	3.99	0.83
$Fe(OH)_3$	4.20	3.45
goethite FeOOH	8.59	7.84
haematite	18.50	16.99
strontianite	2.02	0.44
pH	7.87	5.74

Note: SI - index of saturation

In the second simulation, when the gas was not separated, under partial CO_2 pressure 2,022 MPa and the same temperature of 91°C the result of the simulation is virtually identical. This basically means that even at a sufficient content of carbon dioxide the mineral phases did not reach equilibrium state, and the resulting effect from the point of view of the mineral phases was similar to the one in the first test. High CO_2 content is reflected in the decline in the pH value to 5.74.

Within the production of anthropogenic emissions of carbon dioxide into the atmosphere, we made an estimate of the natural emissions of this gas in Slovakia, which may be considered as natural background from this source.
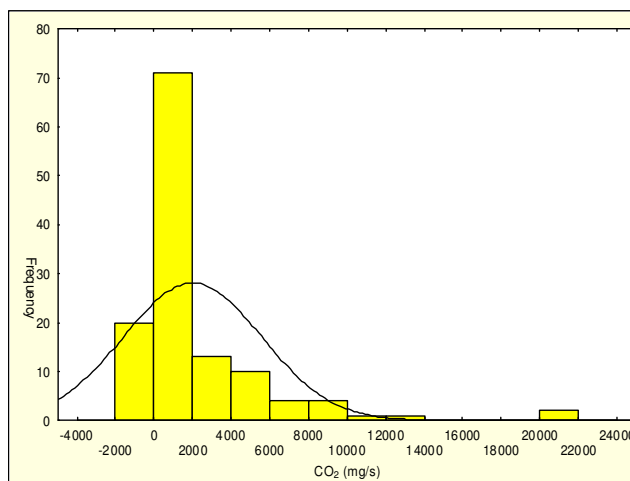
Fig. 5.3.1 Histogram of the distribution of CO_2 production by mineral waters.

Besides organically produced CO_2, CO_2 from soils, CO_2 originating from other natural waters, volcanic activity (in terms of SR is currently extinct) the sources of mineral waters are likely to be its biggest producer.

The estimate of the natural emissions from mineral waters was based on the approach that all the released carbon dioxide, whether for therapeutic purposes when using mineral waters, or stuffed into consumer packaging will ultimately gets into the atmosphere.

An estimate has been made on the basis of the registration of mineral waters ISS (Inspectorate of Spas and Springs) MH SR.

Other sources of information about mineral waters cannot be used in practice. The reason is the lack of the yields of the sources, as one of the parameters, from which the estimate was made. It was based on the formula:

$$MOU = c_{OU} * Q$$

MOU   the amount of carbon dioxide in $mg.s^{-1}$,

c_{OU} the concentration of carbon dioxide ($mg.l^{-1}$) in mineral water,

Q   yield ($l.s^{-1}$) of mineral water source.

Recently on the territory of the Slovak Republic there have been registered more than 1700 sources that meet or comply with the criteria for the indication of the mineral water. The number indicates all registered sources, but not all the existing ones. The situation reflects the status of the registration, which is a long-term issue. The status of many sources is uncertain, some of them have been destroyed, and many have disappeared due to anthropogenic interventions. At many sites effluences of dry CO_2 are known, for instance Vyšné Ružbachy, Pribylina, etc. Determination of free carbon dioxide is also problematic. Another uncertainty can also be a lot of sources, maybe even existing, which have not been registered in the database. Similarly, it is difficult to estimate how much CO_2 is released from the wells with negative piezometric level. To conclude we have to note that a significant factor, such as temperature, was not taken into account for the solubility of CO_2.

The first step was determination of the amount of carbon dioxide in the calculation of the sources monitored by ISS MH SR (126 sources); the total number of sources in the registry is 1,782. Consequently, the amount of carbon dioxide (MOU):

$$MOU = 140,237 * 250.13 = 35,077,480.81 \ mg.s^{-1}$$
$$= 35.078 \ kg.s^{-1} \ CO_2$$

Distribution of the quantities of carbon dioxide, expressed in the form of histograms is documented in Fig. 5.3.1. It is obvious that there are zero values in the file, either because of zero content of CO_2, or absenting yield value (this represents about 12% of the sources). The layout of these quantities is apparently associated with the lognormal distribution with the largest frequency 0 to $2,000 \ mg.s^{-1}$ and with maximum of 20,000-22,000 $mg.s^{-1}$.

For the above considerations, it would be necessary to recalculate the results through a coefficient, which would include the following: incontinuous exploitation, closed boreholes, or boreholes with free water table level, etc. Designed estimation coefficient KCO_2 could be somewhere at the level between 0.5 to 0.6. For the calculation the estimation coefficient 0.55 was used. The result of the MOU after correction is the quantity: MOU = 35.078* 0.55 = 19.3 $kg.s^{-1} \ CO_2$.

If we take into account that in the overall registration of 1782 sources these need to be corrected on the extinct, liquidated and non-registered boreholes, the estimate factor could be in the range K_r = 0.6 to 0.7 (0.65), which implies that the number boreholes 1,782*0.65 = 1,158.

Another coefficient accounted for the fact whether the mineral source has been identified because of the CO_2 content. In such a case the same coefficient K_M = 0.6 to 0.7 (0.65) was used, and the result is 1,158*0.65 = 752 sources on the territory of SR with CO_2.

Of the number of 752 sources those calculated in the first step (126) have to be deducted: 752-126 = 626.

If we take as a representative the samples in the first step (sources yield, CO_2 content), then the final calculation is 626/126 = 4.96. The total estimated amount of carbon dioxide will be then 6*19.3 = 115.8 $kg.s^{-1}$.

This estimated amount, recalculated to one year represents approximately 3.6 million t of carbon dioxide, which is emitted into the atmosphere from the sources of mineral waters in Slovakia.

6. Mineral sequestration of carbon dioxide in a way of carbonatization

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The main objective of technological research was to point out the possibilities of carbon dioxide storing (CO_2) into suitable geological structures, or to demonstrate CO_2 sequestration (disposal) using selected geological materials from specific sites in Slovakia in the way of mineral carbonatization. In the implementation of the experimental work P-T-t parameters (pressure, temperature, time) were simulated under laboratory conditions to determine the options and the potential for CO_2 storage in appropriate petrographic complexes by the method of mineral carbonatization.

The results of experimental works have been used for the calculation of the storage capacity of individual sites with their quantification and sorting in the database.

6. 1 Mineral carbonatization

Mineral carbonatization is a way of CO_2 storing by its fixation in the crystal lattice of stable carbonate minerals, such as calcite, magnesite, dolomite, siderite, etc (Metz et al., 2005). Proposal for sequestration of CO_2 by mineral carbonatization was designed in 1990 in the journal Nature in the contribution of Seifritz (1990) and the first work dealing with the subject was published in 1995 in Energy Journal, by team K. S. Lackner, C. H. Wendt, D. P. Butt, E. L. Joice Jr. and D. H. Sharp. In the article a mineral carbonatization is presented as a safe method of CO_2 liquidation based upon the chemical bonds in raw materials, resulting in formation of solid carbon minerals (Lackner et al., 1995).

In 2005, the method was finally defined in the IPCC Special Report on Carbon Dioxide Capture and Storage, part 7. Mineral carbonatization and Industrial uses of Carbon Dioxide (IPCC, 2005). According to this definition, mineral carbonatization is based on the reaction of CO_2 with oxides resulting in formation of insoluble carbonates. In the course of carbonatization CO_2 reacts with oxides of elements, such as for example Mg, Ca, or Fe, to form carbonates and at the same time heat develops at different levels according to the general equation (IPCC, 2005):
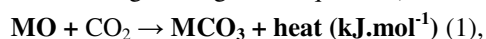
MO + CO_2 → **MCO_3 + heat (kJ.mol^{-1})** (1),
according Bochenczyk et al. 2007:
CaO + CO_2 → **$CaCO_3$ + 179 kJ.mol^{-1}** (2),
MgO + CO_2 → **$MgCO_3$ + 118 kJ.mol^{-1}** (3).

The main advantage of mineral sequestration of CO_2 by the way of carbonatization in high-pressure reactor rests in safe disposal of gaseous carbon dioxide, which is based on the reactions of active compounds in suitable raw mineral materials and rocks with carbon, creating solid products, in which the CO_2 is safely, permanently and stably bound in the newly emerging mineral forms. In this way, from input materials stable carbonates or acidic carbonates evolve, with fixed CO_2 bonds which do not have a negative impact on the environment. Carbonatization reactions, resulting in the emergence of Ca, Mg, or Fe carbonates are predominantly exothermic, which means that the heat generated in the process of carbonatization could be potentially utilised.

The mineral carbonatization in the reactor can be realized in direct and indirect ways. In the direct method the appropriate minerals get into the direct reaction with the carbon dioxide. In the indirect method first the reactive components of suitable materials are extracted or activated and subsequently enter into a reaction with CO_2. In both cases, it is possible to modify the input minerals in mechanical, chemical, physico-mechanical or mutually combined ways with the aim of speeding up the reaction with the carbon dioxide.

Carbonatization of rocks in natural conditions (injection of CO_2 into a suitable ground) is a very slow process, therefore it is necessary to speed up reactions in the reactor technology to optimize all the factors that influence the reactivity of the minerals with CO_2. The result of the reaction of CO_2 with rocks in the reactor during a short period of time (hours to days) are solid amorphous phases and artificially produced minerals containing CO_2 or bonds OH^-, HCO_3^{3-}, CO_3^{2-}, and H_2O in them (Radvanec et al., 2008, Tuček et al., 2008). This process is very close to metamorphic carbonatization, which takes place in the Earth's crust reactions, but also to weathering processes at the surface.

Procedures and experiments with artificial carbonatization from the modern view of industrial CO_2 liquidation were published in the 90ties of the last century in the US (e.g. Seifritz, 1990; Lackner, 1997A; Lackner, 1997B), when from the geological materials (ultramafites, mafites) the attention has been shifted to other appropriate geological materials and gradually transferred to industrial waste,

and an important element of this process has become an issue of economic efficiency. In the following years, the most research has been focused in detection of rapid reaction procedures for characterization of mineral reactants and reaction products, as well as working ranges for the identification and determination of the reaction conditions of experiments.

Up to now the ultramafic, or other rocks from the territory of the Western Carpathians have not been technologically studied as possible experimental material for disposal of industrial CO_2 emissions and for these reasons, the geological–technological research does not exist.

6.2 Procedure and the methodology of techno-
logical research

The technological part was dealt in the scope of the approved project, titled "Quantitative Parameters of Geological Structures, Suitable for CO_2 Storage" and in accordance with criteria of quality management system ISO 9001: 2008 SGIDS, as well as in accordance with the quality requirements as defined in Decree No 51/2008 of the Ministry of Environment of the Slovak Republic.

In the initial stage of work there were taken a total of eighteen samples of geological materials of the mass in the range of 1-15 kg. The samples were classified into four groups according to the mineralogical composition - serpentines (11 samples), amphibolic-chloritic and talc serpentines (2 samples), amphibolite (4 samples) and one sample of basalt.

A scheme of laboratory research of carbonatization using carbon dioxide is shown in Fig. 6.1. From the scheme it follows that the samples underwent crushing, when necessary, grinding up to 1 mm grain. After the sorting process the fraction of +1 mm was completely milled.

Carbonatization testing using a dry method (Fig. 6.1) was carried out in static conditions, dry ground material was in contact with the gaseous carbon dioxide at atmospheric pressure and ambient temperature for a period of two years.

Carbonatization using a wet method was carried out in reactors. The unmodified or modified specimens suspension was subjected to CO_2 action at different P-T-t conditions. The processes of filtration, followed by crystallization were used to verify the bonds of CO_2 in the newly created products (Fig. 6.1-III. Carbonatization by wet method).

According to the scheme in Figure 6.1, after the free drying, all the samples were subjected to the finening up in one to three stages in the jaw crushers, sorting and milling in the Bowl mill to reach a grain below 1 mm. Subsequently, all the samples were homogenized and quartered. The homogenized specimens were prepared for further processing, including wet grain-size distribution analyses.

In the scope of the technical work there was carried out thermal modification of specimens. In selected samples chemical modification was realized in order to acti-

vate or extract Ca, Mg, and Fe components from suitable mineral compounds (e.g. serpentine minerals) or from amorphous mass to accelerate the reactions with CO_2.

The experimental laboratory tests of CO_2 binding to the appropriate components of geological materials were carried out in a glass flow rotary reactor with the parameters: CO_2 pressure ~ 0.1 MPa; ambient temperature ~ 20 up to 100 °C and in a glass oscillating reactor with the parameters: pressure ~ 0.1 up to 0.9 MPa; ambient temperature ~ 20-25 °C.

Simulation of P-T-t conditions of the carbonatization process and testing of CO_2 storage options were made in the laboratory high-pressure reactor PARR 4540 with the following maximum operating parameters: CO_2 pressure 16.5 MPa, temperature up to 250 °C, the speed of the stirrer up to 650 rpm and pH of the environment in the range of 1 to 12, that it is possible to modify by acids < 7 and pH > 7 by hydroxides.

In the laboratory research of mineral sequestration of CO_2 in the reactor, carbon dioxide with a purity of 99.9% was used with a negligible content of nitrogen as the residual gas.

The proof and testing analyses of CO_2 reactivity with the components of the input geological materials were made in the reactors under different initial pressures (from 0.1 to 20 MPa), different temperatures (20 to 100 °C), and various times of exposure to CO_2 action (from 1 to 24 hours).

The grists of different grain size were mixed in the aquatic environment to achieve suspensions with about 150-160 $g.l^{-1}$ densification, which were subsequently subjected to proof and test laboratory analyses of carbon dioxide sequestration in the reactors.

Dynamic conditions of Mg, Ca, or Fe component reactions with CO_2 in aqueous suspensions were ensured in all tests in a high-pressure reactor with a stirrer speed from 150 to 300 rpm.

The pH values of some of the input grist suspensions, in particular, those thermally modified, ranged from 9.0-11.0 at the start of the carbonatization tests. The final parameters of the process such as pressure, temperature, and pH of the suspension after the sequestration of CO_2 were influenced by the process kinetics, i.e. a solution of carbon dioxide in an aqueous environment, as well as the mutual reaction of solid phase with CO_2 and water. The output pH values of the suspensions ranged from 6.5 to 8.0.

The output products of the CO_2 sequestration processes were withdrawn from the reactor (as a whole), or separated by filtering into filter cakes (solid phase) and filtrates (liquid phase), from which subsequently precipitated products containing carbonates were subjected to a drying (50 to 200 °C). Their mass was determined by weighing.

The homogeneous parts of the input specimens and output products after carbonatization or filtration and crystallisation by drying were identified by X-ray diffraction analysis, chemical analyses, and microanalyses to demon-
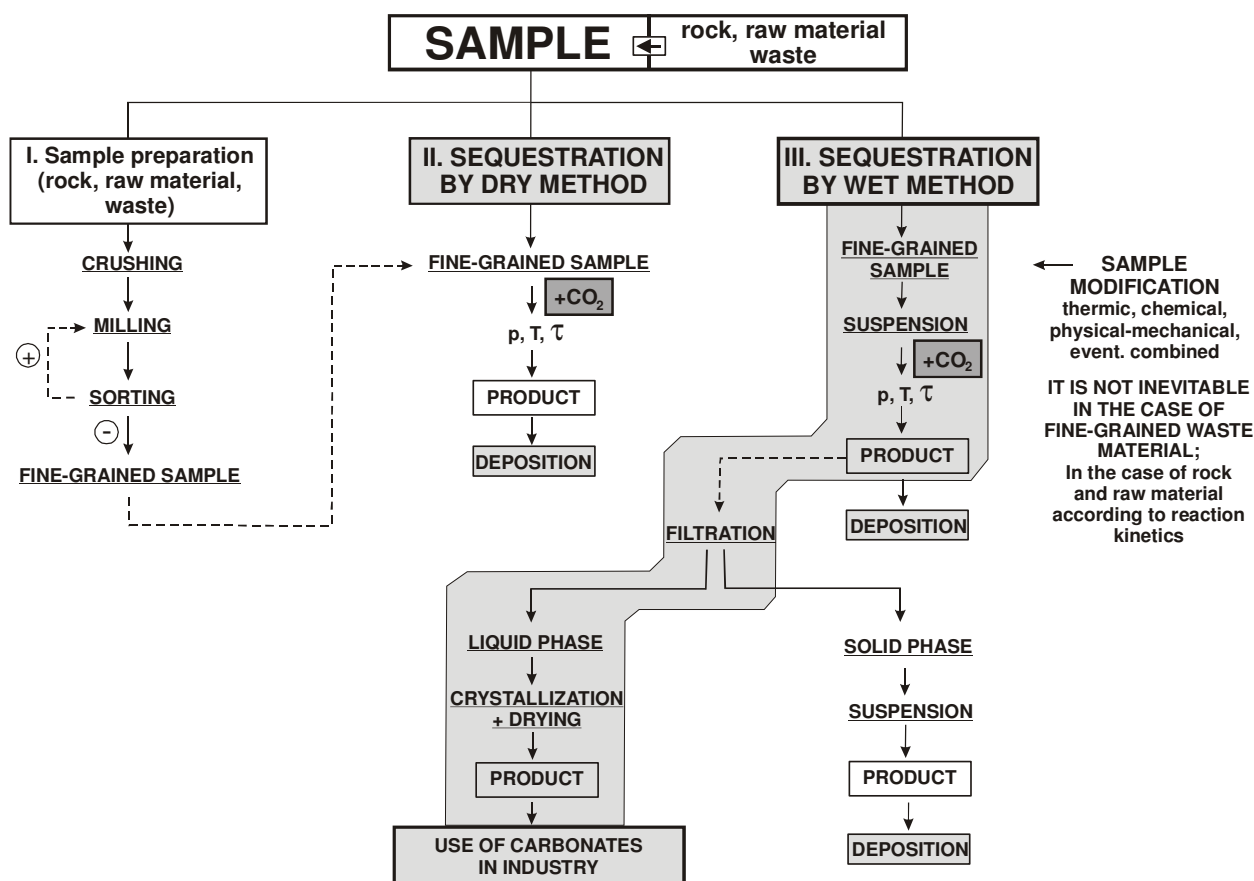
Fig. 6. 1 Scheme of research of samples carbonatization by CO_2 action

strate the binding of CO_2 in solid products. All the chemical analyses were carried out in the SGIDS Geoanalytical Laboratories in Spišská Nová Ves (GAL), which is an accredited testing laboratory under ISO/IEC 17025:2005 and the reference laboratory of the Ministry of Environment of the Slovak Republic for the analysis of the geological materials and rock environment (control laboratories within the meaning of the Decree No. 221/2005 Coll.). In order to determine CO_2 the methods of high-temperature oxidation and volumetric analyses (manometry) were used; CaO and MgO were determined by röntgenfluorescence spectroscopy, FeO by volumetric analysis and the loss on ignition by the gravimetric method. X-ray diffraction analysis of all samples and experimental research work was carried out in the laboratories of SGIDS - Applied Technology of Mineral Resources (ATNS) in Košice, while qualitative mineralogical analysis of the samples was carried out by the X-ray diffraction analysis using apparatus DRON-UM 1 with the sensitivity of detection of approximately 3% under the following conditions: radiation CoKα, Fe-filter, accelerating voltage of 30 kV, the intensity of the current 20 mA, time constant T-2, apertures 2-2 and 1-0.25, shift of the goniometer arm 2°. min^{-1}.

The evaluations of x-ray records were made according to the classic ASTM tables using a special computer programme. This method served for identification of a qualitatively new phases in mineral products; the threshold was a content of about 3%. Semi-quantitative to quantitative representation of the minerals in the carbonatization samples and products was determined by a combination of methods of X-ray diffraction analysis and mineralogical conversion from chemical analyses. In the X-ray diffraction analysis the external standard method was used. In the conversion of the chemical analysis the theoretical chemical composition of the present minerals was applied.

The carbonatization products and non-reacted residue after filtration (filter cake) were photographed in binocular loupe. From these products polished thin sections were made, which were studied in the optical microscope and the electron analyser in order to determine the chemical composition of the newly emerging minerals and undissolved residue. The exact chemical composition of the input samples (powders), all the newly emerging minerals and residue after filtration were detected using Cameca SX 100 device of SGIDS in Bratislava.

The used mineral standards: for the calibration of Ca - wollastonite, Mn - rhodonite, Na - albite, K - orthoclase, Cr - chromite. Synthetic compounds were used for the calibration of the content of Ti, Al, Fe, Mg and BaF_2 for F. The analytical parameters of measurements were accelerating voltage of 15 kV and beam current of 5 nA, when analysing the acid carbonates and carbonates, or 20 nA when analysing silicates and amorphous phases. The beam diameter of 1-7 μm was used for analysing of

silicates depending on the size of the measured objects in the thin section. In the case of the acid carbonates and carbonates the beam diameter of 7 – 20 μm was used. The counting time of each element was 10 s except for F which was counted during 25 s. The detection limit for each element was lower than 0,05% of mass with an error of ±1-sigma.

From the measured results and implemented mineralogic-petrographic calculations the original mineral associations were defined and the associations incurred after the reaction of geological specimens with CO_2.

All the results obtained were processed and evaluated in written, tabulated, graphical and photodocumentary form.

6.3 Characteristics of the input samples of geological materials

The homogeneous parts of the input samples (grit, grist) were subjected to X-ray diffraction analysis and chemical analyses. In Tables 6.1 and 6.2 the chemical and mineral composition of the input samples (recalculated from a combination of the methods of X-ray diffraction analysis and chemical analysis, whereas the theoretical composition of minerals has been used in calculation), as well as sampling sites and their designations are presented.

As aforementioned already, the samples were divided into four groups according to mineralogical composition (Table 6.2): 11 samples containing dominant serpentine minerals ranging from 65.7 to 88.7%, olivine (+pyroxene) in the range from 0% to 25.2%, magnetite (maghemite) from 5.0 to 8.9% and mineral components present in accessory quantities – calcite (0.4-7.9%) and chromite (0.4-0.5%).

In the second group there were two samples: one sample amphibolic-chloritic serpentine with 17.9% of amphibole and 18.2% content of chlorite with serpentine minerals present (47.9%) and a second sample of talc serpentine with 64.5% talc and 14.9% of chlorite content.

The third group (amphibolites) comprised four samples containing plagioclase (29.0-37.2%), chlorite (15.8-34.5%), amphibole (3.8-28.3%) and epidote (0-29.0%).

The fourth group comprised one sample of basalt, consisting of plagioclase (47.1%) pyroxene (38.6%) and olivine (10.8%).

Table 6.2 shows that the first group of samples contained serpentine minerals (according to analysis, in particular lizardite and chrysotile, less antigorite) and olivine (+pyroxene), which bind in the crystal lattice the Mg-component (Mg-oxide from 34.75 to 39.73%); under appropriate P-T-t conditions this component is suitable for reaction with CO_2 creating new mineral compounds - Mg-carbonates (nesquehonite, hydromagnesite, eventually magnesite). According to X-ray diffraction analysis the calcareous component in these samples is bound to calcite.

In the second group the talc and chlorite are the Mg-carriers (Mg-oxide from 30,07 to 33.50%, sample from the Beňuš site), out of a total content the Mg-component is bound to the magnesite and dolomite, and the whole portion of Ca-component is bound to dolomite. In the sample from Filipovo the Mg-component is bound to serpentine minerals and chlorite, the sample doesn't contain carbonate minerals and calcium component is bound to the amphibole.

In the third group (amphibolites) the Mg-component (from 4.09 to 7,81%) is tied chlorite and Ca-component to plagioclase, amphibole (with the exemption of the sample from the site Ostrá); in this sample almost the entire amount of Ca is bound to calcite and only a tiny portion to plagioclase.

The basalt sample from the site Bulhary contains Mg-component bound to pyroxene and olivine, and the calcium component is bound to plagioclase and pyroxene.

6.4 The results of experimental research of mineral carbonatization

The samples contain mineral compounds which bind in their structure the elements such as calcium, magnesium, and iron, which under appropriate temperature-pressure conditions are to bind carbon dioxide (in the case of iron only in the form of Fe^{2+}), with resulting new solid products containing carbonate minerals, in which CO_2 is fixed in the crystal lattice of carbonates and acid carbonates.

In the samples the carriers of Ca component for reaction with CO_2 (the part that is not linked in the input samples to $CaCO_3$) are in particular minerals: plagioclase, amphibole, epidote and pyroxene. Serpentine minerals (mainly lizardite and chrysotile), olivine, pyroxene, chlorite and talc are the carriers of the Mg-component. The Fe^{2+} -component present in chlorite and olivine is potentially suitable for reaction with carbon dioxide.

Implementation of experimental work and research of mineral sequestration of CO_2 process with results achieved for two selected pilot sample groups of serpentines is documented in Chapter 6.4.1.

6.4.1 Site Hodkovce - Serpentines

From the site Hodkovce two specimens were sampled, designated HO-1 and HO-2. Their chemical and mineral composition is very close (Tables 6.1 and 6.2). In both samples, the content of the minerals which bind Mg-component (lizardite and olivine+pyroxene) reaches 90.2% and 90.4% but slightly differs only by the proportion of the above mentioned minerals. The sample HO-1 contains about 2.7% more olivine + pyroxene as the sample HO-2; the sample HO-2 contains about 2.5% more lizardite (serpentine mineral) than sample HO-1. The contents of Ca and Fe^{2+} are low, i.e. CaO below 0.72% and FeO below 0.15%, whereas the Ca-component in both samples is bound to insignificant quantities of calcite (0.4-1.3%).

Tab. 6.1 Chemical composition of input samples

Nr.	Site	Sample	Chemical compound (% by weight)												
			SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	Na_2O	K_2O	P_2O_5	Cr_2O_3	Loss by ign.
Serpentines															
1.	Hodkovce	HO-1	40.21	0.02	0.94	7.27	0.15	0.72	**36.06**	0.08	<0.01	<0.01	<0.01	0.298	14.12
2.	Hodkovce	HO-2	40.01	0.05	0.77	8.04	0.11	0.24	**36.73**	0.07	<0.01	0.02	0.01	0.334	13.44
3.	Rudník	RU-1	37.87	0.06	2.02	6.15	0.22	4.44	**34.75**	0.11	0.01	<0.01	0.01	0.364	13.98
4.	Rudník	RU-2	39.62	0.05	1.71	6.36	0.11	2.02	**36.47**	0.07	<0.01	<0.01	<0.01	0.355	13.03
5.	Jasov	JA-1	40.61	0.06	2.46	5.74	1.09	2.61	**36.23**	0.15	0.06	0.01	<0.01	0.363	11.41
6.	Dobšiná	S-1	38.82	0.04	1.30	8.02	1.05	1.62	**36.09**	0.14	0.03	0.05	0.01	0.359	13.24
7.	Komárovce	KO-1/2	37.79	0.01	0.58	7.75	-	0.59	**39.72**	0.11	0.02	0.01	<0.01	0.361	12.82
8.	Komárovce	KO-1/11	36.93	<0.01	0.42	6.94	-	1.41	**38.64**	0.10	0.03	0.02	<0.01	0.321	14.96
9.	Komárovce	KO-1/16	38.66	0.01	0.77	7.73	-	0.93	**39.73**	0.11	0.02	<0.01	<0.01	0.364	11.43
10.	Breznička	BR-1	39.30	0.04	1.45	8.39	1.27	1.07	**36.90**	0.11	<0.02	<0.01	<0.01	0.380	11.90
11.	Miglinc	MI-1	39.20	0.04	2.12	8.50	1.75	0.70	**35.80**	0.11	0.46	0.15	0.04	0.370	12.10
Amphibolic–chloritic and talc serpentines															
12.	Filipovo	Fl-6	36.70	0.72	4.13	17.20	6.43	2.47	**30.07**	0.23	0.05	0.02	0.06	0.309	7.06
13.	Beňuš	BE-1	40.50	0.19	3.40	9.08	5.53	1.14	**33.50**	0.12	0.01	0.02	0.02	0.458	11.20
Amphibolites															
14.	Ostrá	OS-1	45.53	2.10	16.19	13.20	7.42	6.25	**6.03**	0.16	4.40	0.31	0.21	0.016	5.16
15.	Babina	BA-1	46.86	1.98	19.01	9.59	4.07	10.60	**4.09**	0.11	4.39	0.13	0.16	0.014	2.61
16.	Šemša	ŠE-1	48.65	1.07	13.77	12.90	7.19	8.57	**7.81**	0.20	3.87	0.50	0.08	0.017	2.42
17.	Jaklovce	JK-1	47.90	1.65	14.80	11.10	6.91	10.30	**6.99**	0.18	3.44	0.22	0.14	0.335	2.73
Basalt															
18.	Bulhary	BU-1	45.10	2.15	16.20	9.28	5.82	10.30	**8.95**	0.16	4.28	2.25	0.58	0.278	0.42

Note: Fe₂O₃ total content;

Tab. 6.2 Mineral composition of input samples

Nr.	Site	Sample	Mineral compound (% by weight)							
Serpentines			**serpentine minerals**	**olivine + pyroxene**	**magnetite (maghemite)**	**calcite**	**chromite**			
1.	Hodkovce	HO-1	77.8	12.6	7.9	1.3	0.4			
2.	Hodkovce	HO-2	80.3	9.9	8.9	0.4	0.5			
3.	Rudník	RU-1	67.6	19.0	5.0	7.9	0.5			
4.	Rudník	RU-2	76.6	12.5	6.8	3.6	0.5			
5.	Jasov	JA-1	78.5	9.7	6.6	4.7	0.5			
6.	Dobšiná	S-1	88.7	-	7.9	2.9	0.5			
7.	Komárovce	KO-1/2	65.7	25.2	7.5	1.1	0.5			
8.	Komárovce	KO-1/11	87.0	3.6	6.4	2.5	0.5			
9.	Komárovce	KO-1/16	70.4	19.8	7.6	1.7	0.5			
10.	Breznička	BR-1	85.9	3.5	8.2	1.9	0.5			
11.	Miglinc	MI-1	86.6	3.2	8.5	1.2	0.5			
Amphibolic–chloritic and talc serpentines			**serpentine minerals**	**chlorite**	**amphibole**	**magnetite (maghemite)**	**chromite**	**talc**	**magnesite**	**dolomite**
12.	Filipovo	FI-6	47.9	18.2	17.9	15.5	0.5	-	-	-
13.	Beňuš	BE-1	-	14.9	-	7.5	0.7	64.5	8.7	3.7
Amphibolites			**plagioclase**	**chlorite**	**amphibole**	**epidote**	**calcite**	**quartz**	**mica**	**oxides Fe, Ti**
14.	Ostrá	OS-1	37.2	34.5	3.8	-	10.3	6.9	3.3	4.0
15.	Babina	BA-1	37.1	20.9	13.0	29.0	-	-	-	-
16.	Šemša	ŠE-1	32.7	19.4	21.4	23.2	-	-	-	3.3
17.	Jaklovce	JK-1	29.0	15.8	28.3	22.7	1.7	-	-	2.5
Basalt			**plagioclase**	**pyroxene**	**olivine**	**oxides Fe, Ti**	**calcite**			
18.	Bulhary	BU-1	47.1	38.6	10.8	3.4	tr.			

Note: tr. – traces (< 1%)

6.4.1.1 Laboratory tests of carbonatization using HO-2 sample material

The HO-2 sample has a considerable potential for sequestration, because it contains 36,73% of Mg-component expressed as MgO; to speed up the reaction of this compound with CO_2 it is necessary to fine down the sample in order to increase the specific surface area, i.e. to release the Mg-component from lizardite and olivine +pyroxene by mechanical modification (crushing, grinding and sorting).

Mechanical modification of the sample

The HO-2 sample was collected in piece, the dimension of the largest pieces of the sample was up to 150 mm. The sample was air-dried and than finened in three stages on the grain of about 1 mm, homogenized and quartered. The prepared grit was subjected to wet granulometric analysis (Table 6.3). In the next procedure the grit was ground for a period of 1, 2, and 3 hours, in order to achieve an increase in specific reactive surface and Table 6.4 presents granulometric analyses of the grit tests. The mass yield of each granulometric class, the total residue after sieving are related to dry sample state.

Table 6.3 shows that in the HO-2 sample the 97.87% of the grit is below 1 mm, while the proportion of classes below 0.1 mm is low – 26.04%. The content of the finest granulometric class (-0.02 mm) is also small (17.47%).

Tab. 6.3 Wet granulometric analysis of the grit of the HO-2 sample

Granulometric class (mm)	Mass yield in %		
	class	total residue	undersize in total
+ 1.0	2.13	2.13	-
0.5-1.0	29.07	31.20	97.87
0.2-0.5	30.33	61.53	68.80
0.1-0.2	12.43	**73.96**	38.47
0.063-**0.1**	4.07	78.03	**26.04**
0.045-0.063	2.47	80.50	21.97
0.020-0.045	2.03	82.53	19.50
-0.020	17.47	-	17.47
In total	100.00	-	-

Tab. 6.4 Wet granulometric analysis of the HO-2 sample grit

Granulometric class (mm)	Mass yield in %		
	grit grinding 1 hour	grit grinding 2 hours	grit grinding 3 hours
0.1-1.0	40.90	19.87	7.27
0.063-0.1	12.00	16.20	17.77
0.045-0.063	5.70	7.47	7.97
0.020-0.045	12.67	17.80	20.67
-0.020	28.73	38.66	46.32
In total	100.00	100.00	100.00

The grist samples after period of 1, 2, and 3 hours of grinding contain 59.1%; 80.13% and 92.73% below 0.1 mm, respectively, whereas the proportion of the finest granulometric fraction - 0,02 mm is increasing on about 10% to almost 5%, i.e. in the order of 28.73%; 38.66% and 46.32%.

The samples of grit and three grists of the above granulometric classes were placed in the dry and wet state into a sealed glass container for two years, whereas the carbon dioxide was replenished in the container on a daily basis in the working days to maintain the gaseous carbon dioxide at atmospheric pressure (approximately 0.1 MPa).

By comparing the X-ray diffraction patterns of the grit and three grists, or their initial masses, and after two years of experiments, it appears that under these conditions there was no reaction between CO_2 and the Mg-component of mineral elements, which is confirmed also by zero increase in the weight of the samples.

For the above reasons there were carried out a number of laboratory tests of carbonatization, on both mechanically or chemically modified HO-2 sample (650 °C for a period of 1 hour) to demonstrate the creation of new products, especially the Mg-carbonates, in which the CO_2 is bound in the nesquehonite (its crystallization by drying at 50 °C), or hydromagnesite (crystallization by drying at 200 °C) after carbonatization in the reactor.

The proof tests of mineral sequestration of CO_2 were implemented with the HO-2 sample suspension in the ratio of solid phase/the liquid phase (water) 1:5, with the solid phase formed by the grit samples below 1 mm or grist (grit ground for three hours) in combination with a thermal activation of grit, and grist samples. The tests were carried out under the carbonatization input CO_2 pressures 0.3; 0.6 and 0.9 MPa at ambient temperature (~ 22 °C) during one or several hours in the glass horizontally oscillating reactor.

The best results were achieved under CO_2 input pressure of 0,3 MPa at room temperature of the laboratory environment (suspension) for 1 hour duration of carbonatization) with the grit sample thermally activated. When the filtrate dried at 50 °C the new product precipitated with the dominant highly-pure nesquehonite. The product in question was identified by X-ray diffraction analysis (Fig. 6.2-6.5), thermal analysis (Fig. 6.3-Table 6.6) and chemical analysis (Table 6.7).

The precipitated new product contained 97.5% nesquehonite; 0.9 % calcite and 1.6 % other oxides (Si, Al, ...). The thermal analysis, which is characterized by endothermic effects, detected (Fig. 6.3-6.6.), that under the temperature interval of 105-360 °C the product released two molecules of water with a loss in mass of 34.9 % (39.05% in theory).

In the temperature range 360-460 °C it occurs the release of one molecule of water from the crystal lattice of nesquehonite. At the interval 460-580 °C the destruction of the crystal lattice occurred, with a loss of 31.3% of mass for the range of 360-580 °C (31.81% in theory).

Above 580 °C the amorphous MgO crystallized turning to periclase while the weight loss in the range 580-1,000 °C is negligible - 1.4%. The total loss in the temperature interval of 105-1,000 °C is 67.6 % (70.86 % in theory).

As regards the quality of the carbonatization product obtained by the filtrate drying at 200 °C, a new highly-pure product with a dominant content of hydromagnesite precipitated out, and the best results were achieved under the CO_2 input pressure of 0.3 MPa and the environment temperature of 22 °C, with the carbonatization duration of 1 hour and the thermally activated grit sample.

This product was identified by X-ray diffraction analysis (Fig. 6.4-Table 6.8), thermal analysis (Fig. 6.5-Table 4.3) and chemical analysis (Table 6.10).

The precipitated new product contained 97.4% of hydromagnesite; 1.6 % of calcite and 1.0% of other oxides (Si, Al, ...). The thermal analysis, which is also characterized by endothermic effects, detected (Fig. 6.5-Tab. 4.3), that up to a temperature of 360 °C the product released four molecules of water manifested in 19.0% decrease in mass (22.24% in theory).

Fig. 6.2 X-ray diffraction record of the product precipitated from the filtrate (drying at 50 ºC) with a dominant nesquehonite prepared by carbonatization from mechanically and thermally activated HO-2 sample

In the temperature range of 360-460 °C it occurred a release of OH functional group from the crystal lattice of hydromagnesite, while within the interval of 460-580 °C the disintegration of the crystal lattice occurred, with the release of CO_2 accompanied by a mass loss of 35.1 % for the range of 360-580 °C (in theory, 36.25 %).
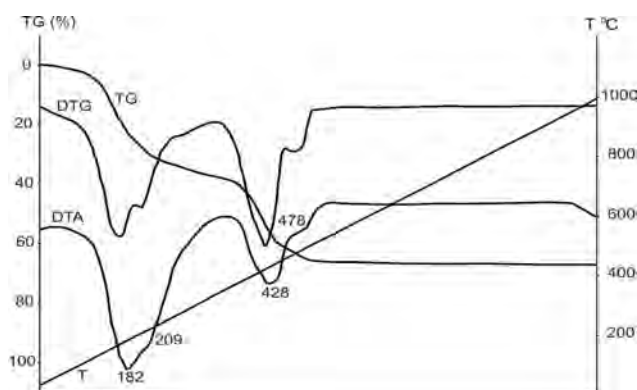
Fig. 6.3 Thermal analysis of the precipitated product from the filtrate (drying at 50 ºC) with a dominant nesquehonite prepared by carbonatization from mechanically and thermally activated HO-2 sample

Above 580 °C the gradual crystallization of the amorphous MgO turning to periclase occurred, while the mass loss in the interval of 580-1,000 °C was negligible – 2.0%. The total loss in the temperature interval of 105-1000 °C was 56.1% (58.49% in theory).

Simulation of P-T-t conditions of the carbonatization process and testing of CO_2 storage options in the newly created carbonate product in the first set of experiments in the laboratory was carried out in high-pressure reactor PARR, model 4540. The focus was in the effect of the CO_2 input pressure increase upon the increments in the mass yield of the new (precipitated) product containing Mg-carbonates of the grit samples HO-2 at room temperature (22 °C), within one hour of the CO_2 action and constant stirrer speed (150 rpm); the results are shown in Table 6.11.

The initial temperature of the suspensions under the CO_2 input pressures 8.0 MPa and more gradually increased in all other samples tested and ranged from 31 to 35 °C due to the achievement of a critical state of CO_2 (the interface between the gaseous and liquid state of the carbon dioxide is lost at a temperature of 31.1 °C and a pressure of 7.39 MPa). It is difficult to achieve this state, in terms of time-consuming, economic as well as technical point of view.

Table 6.11 shows that the values of increment in the mass yield of the newly formed product containing hydromagnesite and amorphous substance are low and very close (0.32-0.46%), while taking into account the above, the value of the CO_2 pressure 6 MPa was chosen as optimal in regard to achieved increment in the mass of new product and hydromagnesite content in the precipitated product.

Tab. 6.5 The measured values of the X-ray diffraction analysis and table values of nesquehonite (to image 6.2)

Number	Measured values			Table values	
	angle	d (nm)	I	d (nm)	I
1	13.750	0.644	100.00	0.648	100.00
2	23.210	0.383	85.57	0.385	75.00
3	24.940	0.357	7.23	0.359	8.00
4	27.670	0.322	11.61	0.323	20.00
5	29.600	0.302	13.34	0.303	30.00
6	30.140	0.296	1.97	0.298	6.00
7	32.340	0.277	3.39	0.278	10.00
8	34.320	0.261	3.31	0.261	55.00
9	35.920	0.250	25.54	0.251	6.00
10	41.650	0.217	12.58	0.218	2.00
11	42.000	0.215	4.92	0.216	4.00
12	45.000	0.201	4.60	0.202	8.00
13	47.320	0.192	22.02	0.193	16.00

Heading row spanning: Hodkovce 2 – nesquehonite

Tab. 6.6 The measured values of the thermal analysis and table values of nesquehonite (to image 6.3)

Thermal analysis of the product with dominant nesquehonite content – measured values							
Endotherm 1 (°C)				Endotherm 2 (°C)			
start	peak	finish	mass loss	start	peak	finish	mass loss
80	182	280	34.90%	280	428	520	31.40%
Thermal analysis of nesquehonite – table values							
Endotherm 1 (°C)				Endotherm 2 (°C)			
start	peak	finish	mass loss	start	peak	finish	mass loss
100	200	300	39.04%	300	425	550	31.82%

Tab. 6.7 Chemical and mineral composition of the precipitated product containing nesquehonite

Compound	Product	% of compound content by weight					
		SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	CO_2
chemical	precipitated from filtrate	0.99	0.04	0.16	0.50	28.4	31.4
mineral		nesquehonite 97.5%; calcite 0.9%; oxides Si, Al,... 1.6%;					
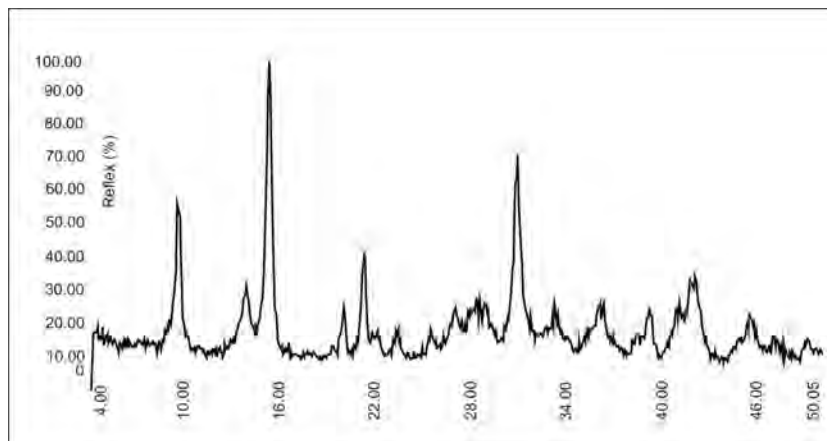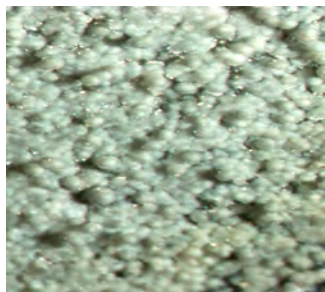
Fig. 6.4 X-ray diffraction record of the precipitated product from the filtrate (drying at 200 ºC) with a dominant content of hydromagnesite prepared by carbonatization from mechanically and thermally activated HO-2 sample
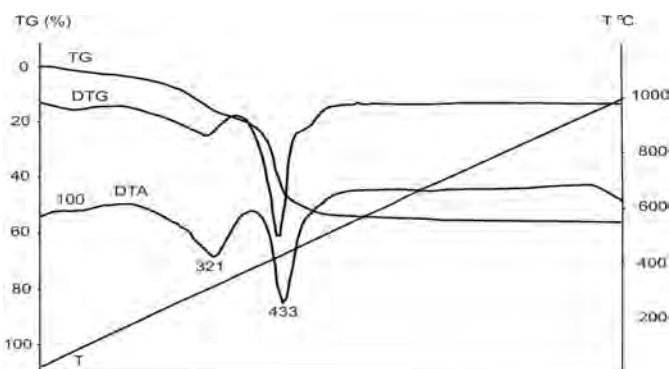
Fig. 6.5 Thermal analysis of the precipitated product from the filtrate (drying at 200 ºC) with a dominant content of hydromagnesite prepared by carbonatization from mechanically and thermally activated HO-2 sample

Tab. 6.8 The measured and table values of hydromagnesite from the X-ray diffraction analysis (to Fig. 6.4)

	Hodkovce 2 – hydromagnesite				
Number	Measured values			Table values	
	angle	d (nm)	I	d (nm)	I
1	9.580	0.923	53.89	0.918	40.00
2	13.800	0.642	31.70	0.644	40.00
3	15.250	0.581	100.00	0.579	100.00
4	19.850	0.447	22.40	0.447	20.00
5	21.190	0.419	41.49	0.421	20.00
6	21.980	0.404	18.44	0.405	5.00
7	23.260	0.382	16.71	0.381	10.00
8	25.390	0.351	19.09	0.350	10.00
9	26.850	0.332	23.63	0.331	30.00
10	28.120	0.317	25.57	0.315	5.00
11	28.780	0.310	26.87	0.309	5.00
12	30.780	0.290	63.76	0.290	90.00
13	33.180	0.270	26.72	0.269	30.00
14	35.920	0.250	26.22	0.250	30.00
15	38.230	0.235	17.50	0.235	5.00
16	39.100	0.230	25.07	0.230	30.00
17	40.990	0.220	27.37	0.220	10.00
18	41.780	0.216	32.99	0.215	50.00
19	45.500	0.199	22.33	0.199	20.00

Tab. 6.9 Measured and table values of hydromagnesite thermal analysis (to Fig. 6.5)

Thermal analysis of the product with dominant hydromagnesite content – measured values							
Endotherm 1 (ºC)				Endotherm 2 (ºC)			
start	peak	finish	mass loss	start	peak	finish	mass loss
105	321	360	17.10%	360	433	540	35.10%
Thermal analysis of hydromagnesite – table values							
Endotherm 1 (ºC)				Endotherm 2 (ºC)			
start	peak	finish	mass loss	start	peak	finish	mass loss
200	340	400	21.92%	450	500	570	36.40%

Tab. 6.10 Chemical and mineral composition of precipitated product with hydromagnesite content

Compound	Product	% of compound content by mass					
		SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	CO_2
chemical	precipitated from filtrate	0.94	0.02	0.06	0.93	42.0	37,4
mineral		hydromagnesite 97.4%; calcite 1.6%; oxides Si, Al,... 1.0%;					

Tab. 6.11 Laboratory tests of CO2 sequestration at temperature of 22 ºC, using HO-2 grit, the duration of CO_2 action for 1 hour, at 150 revolutions of stirrer per min and at various pressures of CO_2

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 0.34	hydromagnesite (57%), AF
4.0	+ 0.32	hydromagnesite (48%), AF
6.0	**+ 0.46**	**hydromagnesite (64%), AF**
8.0	+ 0.46	hydromagnesite (65%), AF
10.0	+ 0.38	hydromagnesite (46%), AF
12.0	+ 0.46	hydromagnesite (44%), AF

Note: AF – amorphous phase

Thermal modification of sample

Other experiments were designed primarily to increase the values of the mass yield of new products after thermal modification of samples grit (thermal activation at 650 °C during one hour), the increasing input pressure of CO_2 and ambient temperature (22 °C), within one hour of the CO_2 action and constant stirrer speed (150 rpm). The results are shown in Table 6.12.

Tab. 6.12 CO_2 sequestration in laboratory tests using thermally modified grit of the HO-2 sample at T = 22 °C, the duration of CO_2 action 1 hour, stirring speed - 150 rpm and different CO_2 pressures

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 5.98	hydromagnesite (75%), AF
4.0	+ 7.01	hydromagnesite (78%), AF
6.0	**+ 9.16**	**hydromagnesite (84%), AF**
8.0	+ 9.58	hydromagnesite (85%), AF
10.0	+ 8.35	hydromagnesite (82%), AF
12.0	+ 9.32	hydromagnesite (76%), AF
14.0	+ 9.09	hydromagnesite (75%), AF
15.0	+ 9.72	hydromagnesite (87%), AF

Note: AF – amorphous phase

Table 6.12 shows that the value of the increments in the mass yield of the newly formed product containing hydromagnesite and amorphous substance are in the range of 5.98%-9.72%. In this case the initial pressure 6 MPa was chosen as optimal, because the increment in the mass yield of new product from the pressure of 6 MPa till 15MPa was negligible (+ 0.56%).

The comparison between the values in Tables 6.11 and 6.12 shows that the increment in the mass yield of a new Mg-carbonate product in the case of the thermally modified grit is generally higher in the range from about 5.5 to 9.2% compared to the original grit, which is related to the destruction of crystal lattice (in particular lizardite) due to heat action at 650 °C, when the release of chemically bound water occur along with activation of the Mg-component for reaction with CO_2.

The carbonatization experiments were also aimed in the effect of increased laboratory environment/suspension temperature (40 °C) upon thermally activated grit, at the gradually increased CO_2 pressure, during one hour exposure to CO_2 and constant stirrer speed (150 rpm); the results are shown in Table 6.13.

Tab. 6.13 Sequestration of CO_2 in laboratory tests using thermally modified grit of the HO-2 sample at T = 40 ºC, the duration of CO_2 action 1 hour, stirring speed - 150 rpm and different CO_2 pressures

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 6.55	hydromagnesite (86%), AF
4.0	+ 9.38	hydromagnesite (86%), AF
6.0	**+ 9.47**	**hydromagnesite (85%), AF**
8.0	+ 9.19	hydromagnesite (84%), AF
10.0	+ 8.69	hydromagnesite (83%), AF
12.0	+ 9.88	hydromagnesite (87%), AF

Note: AF – amorphous phase

Table 6.13 shows the values of the mass increments of the newly formed product containing hydromagnesite and amorphous substance ranging between 6,55-9,88%; in this case the initial CO_2 pressure 6 MPa was chosen as the optimal one, because the increment in the mass yield of the new product from the pressure of 6 MPa till 12 MPa was negligible (+ 0.41%).

By comparing the results in Table 6.12 and 6.13, it appears that the increased temperature of the reaction environment (suspension) from 22 to 40 °C did not produce a significant increase in the mass yield of the new products when changing the input pressure of CO_2, which is advantageous from an economic point of view, and for these reasons, further experiments were carried out at room temperature.

Due to the fact that after carbonatization in the previous tests the increments in the mass yield of the new product containing hydromagnesite reached only up to 10 %, there were carried out three sets of tests with the finest thermally modified grist (Table 6.4 - grist ground for 3 hours) under systematically altered CO_2 pressures during 1, 2 and 3 hours of CO_2 action, constant stirrer speed (150 rpm) and ambient laboratory temperature; the results are indicated in Tables 6.14, 6.15 and 6.16.

From the Tables 6.14 6.15 and 6.16 it follows, that the CO_2 input pressure of 2 MPa with extending the period of carbon dioxide action from 1 to 3 hours the increment in the mass yield of the Mg-carbonate product grows on the value by about 2% of the mass, i.e. in the order of 13.42%; 15.52% and 17.94%. For other values of CO_2 input pressure (from 4 to 10 MPa) with extending the period of carbon dioxide action from 1 to 3 hours the average value of the increment on mass yield of the new product containing hydromagnesite grows in the order of approximately 18%; 20% and 23%, with the

highest growth achieved at optimal CO_2 pressure 6 MPa - 24,36% (Table 6.16).

Accounting for the fact that the reactivity of carbon dioxide with an activated Mg-component in the HO-2 sample is also affected by dynamic environmental conditions (suspension mixing), the CO_2 sequestration tests were made using the finest thermally modified grist (grinding for 3 hours), for a period of 1 hour of CO_2 action at room temperature, in the optimal carbon dioxide pressure of 6 MPa and various speeds of the stirrer (Table 6.17).

Tab. 6.14 Sequestration of CO_2 in laboratory tests using the HO-2 sample grist thermally activated at T = 22 °C, the duration of CO_2 action was 1 hour, stirring speed - 150 rpm and different CO_2 pressures.

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 13.42	hydromagnesite, AF
4.0	+ 17.88	hydromagnesite, AF
6.0	+ 18.48	hydromagnesite, AF
8.0	+ 18.88	hydromagnesite, AF
10.0	+ 17.80	hydromagnesite, AF

Note: AF – amorphous phase

Tab. 6.15 Sequestration of CO_2 in laboratory tests using the HO-2 sample grist thermally activated at T = 22 °C, the duration of CO_2 action was 2 hours, stirring speed - 150 rpm and different CO_2 pressures.

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 15.52	hydromagnesite, AF
4.0	+ 20.52	hydromagnesite, AF
6.0	+ 20.14	hydromagnesite, AF
8.0	+ 20.02	hydromagnesite, AF
10.0	+ 19.34	Hydromagnesite, AF

Note: AF – amorphous phase

Tab. 6.16 Sequestration of CO_2 in laboratory tests using the HO-2 sample grist thermally activated at T=22 °C, the duration of CO_2 action was 3 hours, stirring speed - 150 rpm and different CO_2 pressures.

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 17.94	Hydromagnesite, AF
4.0	+ 24.20	Hydromagnesite, AF
6.0	+ 24.36	Hydromagnesite, AF
8.0	+ 23.26	Hydromagnesite, AF
10.0	+ 22.24	Hydromagnesite, AF

Note: AF – amorphous phase

The stirrer speed must not be too low (in order to avoid settling of the solid phase at the bottom of the reaction vessel), but also not to high, to avoid turbulence and splashing the solid phase of the suspension on the walls of the reaction vessel.

Tab. 6.17 Sequestration of CO_2 in laboratory tests using the HO-2 sample grist thermally activated at T =22 °C, CO_2 pressure was 6 MPa, the duration of CO_2 action was 1 hour, varied stirring rotary speed

Stirrer rotations (rot.min^{-1})	Increment in the mass yield (%)	Minerals in new product
100	+ 16.60	hydromagnesite, AF
200	+ 21.00	hydromagnesite, AF
300	+ 24.78	hydromagnesite, AF
400	+ 24.90	hydromagnesite, AF
500	+ 23.52	hydromagnesite, AF

Note: AF – amorphous phase

Table 6.17 indicates that increasing in the mass yield of the Mg-carbonate product is stable at a speed of suspension mixing from 300-400 rpm. By comparing the values in Tables 6.14 and 6.17 we can state that at the CO_2 input pressure of 6 MPa and its one hour action, the increment in the mass yield of the new product containing hydromagnesite was 18.48% (150 rpm), 24.78% (300 rpm), i.e. more than 6%. The comparable value of the increment was reached under the optimal pressure of CO_2 and its 3-hour action at half mixing speed (150 rpm) – 24.36% (Table 6.16).

Chemical modification of the samples

In addition to the mechanical and thermal modifications of the samples, there is a third way to activate the appropriate components (Ca, Mg, and Fe components) of the mineral input samples for CO_2 sequestration - chemical modification, i.e. extraction of mineral components that bind the above compounds, using acids or hydroxides. In our case, the Mg-component bound to the lizardite and olivine+pyroxene is extracted using, for example, hydrochloric acid or sodium hydroxide, with the consequent effects of CO_2 on chloride or magnesium hydroxide according the reaction formula below:

extraction: $MgO (s) + 2 HCl (l) \rightarrow Mg(Cl)_2 (l) + H_2O$ (4),

carbonatization: $Mg(Cl)_2 (l) + H_2O + CO_2 (g) \rightarrow MgCO_3 (s) + 2 HCl (l)$ (5),
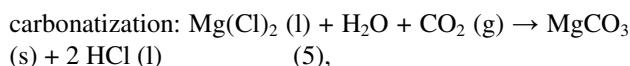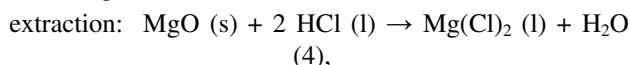
whereas the hydrochloric acid regenerates after carbonatization, or

extraction: $MgO (s) + 2 HCl (l) \rightarrow Mg(Cl)_2 (l) + H_2O$ (6),

precipitation: $Mg(Cl)_2 (l) + 2 NaOH (l) \rightarrow Mg(OH)_2 (s) + 2 NaCl (l)$ (7),

carbonatization: $Mg(OH)_2 (s) + CO_2 (g) \rightarrow MgCO_3 (s) + H_2O$ (8).
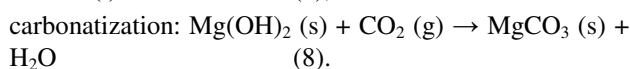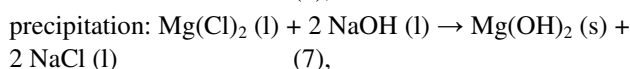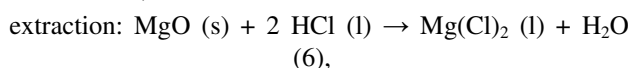
In the first case, the environment is strongly acidic (pH =1-2), and this two-stage "acid way" must meet strict technical requirements and instrumentation, and envi-

ronmental protection. In the latter case, the amount of sodium hydroxide neutralizes the excessive non-reacted hydrochloric acid with consequent formation of NaCl solution according to the equation: HCl + NaOH → NaCl + H$_2$O at pH = 6.5/7.5, while the magnesium hydroxide precipitate has to be washed and must be decanted from the substance, because in a subsequent step the CO$_2$ reacts with Na-ion preferably with the formation of undesirable sodium carbonates and thus contaminates the ultimate Mg-carbonate product.

The liquid phase in Mg-component extraction from the input material sample was primarily 30% solution of hydrochloric acid and 10% solution of sodium hydroxide. The Mg-component extraction tests from the appropriate minerals (in particular, serpentine) present in the input sample were carried out in a glass flow rotary reactor for a period of one or more hours at a temperature of environment 22 °C and 100 °C.

A set of experiments was carried out only with the grit sample of HO-2 (Table 6.3), i.e., without mechanical modifications of grinding within the three-stage process (extraction - precipitation - carbonatization). In the first three experiments hydrochloric acid was used to extract Mg-component from the grit, in a period of 1, 2 and 3 hours at 22 °C, followed by precipitation, washing and decantation with subsequent carbonatization at a pressure of 6 MPa with CO$_2$ action of 1 hour at a temperature of 22 °C. In the other three experiments the conditions were the same, but with the extraction at 100 °C; the obtained results are shown in Table 6.18.

The results of Table 6.18 show that extending the time of Mg-component extraction from the minerals in the grit of the HO-2 sample from one to three hours leads to its content increase in the solution; in other words the content of the bound component in the filter cake is being reduced in the order 25.7%, 22.8% and 21.6% at a temperature of 22 °C, or 19.6%, 14.1 % and 11.0% at extraction temperature of 100 °C, i.e. the Mg-component extraction at a higher temperature is significantly more effective.

According to X-ray diffraction analysis even after three hours extraction at 22° C the filter cake contains a part of the intact lizardite. After the carbonatization of the precipitate in the high-pressure reactor for one hour at a CO$_2$ pressure of 6 MPa the newly created hydromagnesite products contained bound carbon dioxide from 10.3 to 14.7%, halite and iowaite, which binds Fe^{3+} in its structure.

According to the X-ray diffraction analysis patterns, after the extractions at 100 °C the filter cakes included also intact part of lizardite and amorphous substance. After the carbonatization of the precipitate at CO$_2$ input pressure of 6 MPa the precipitates included new hydromagnesite product binding carbon dioxide from 30.3 to 31.1%, i.e. the product containing approximately 80% of hydromagnesite and halite.

In order to avoid the process of precipitation in a three step process (extraction – precipitation – carbonatization) three experiments were carried out, in which the suspen-

sion of the HO-2 sample was directly exposed to 30% sodium hydroxide solution (extraction reagent) during 1, 2 and 3 hours at a temperature of 22 °C, followed by filtration, and the solid residue included the proportion of non-reacted lizardite and amorphous solid phase. In the reactor the filtrate (liquid phase) was exposed to carbon dioxide action for one hour at the CO$_2$ input pressure of 6 MPa and ambient temperature of 22 °C. The increments in the mass yield of the new products were high and ranged from 37.64% to 49.64% (preferential binding to Na-component from the added extraction reagent with CO$_2$), while according to the X-ray diffraction analysis the products included wegscheiderite and nahcolite (hydrocarbons and carbonates of sodium), brucite (magnesium hydroxide) and giorgiosite (magnesium carbonate).

The experiment with the sample of the modified grist (activated only during the three hours grinding) was carried out in two stages according to the "acid extraction method", whereas the suspension of the solid phase (grist samples): the liquid phase (water) = 10 g: 50 ml, was bathed in 20 ml of concentrated HCl. For one hour this mixture was mixed at 100 °C in rotary glass reactor for the purpose of extraction of the Mg-component and formation of magnesium chloride. After the extracting the suspension was filtered and divided to the filter cake containing amorphous phase + relics of lizardite, and the filtrate. The filtrate was subdued to CO$_2$ action with the input pressure of 6 MPa in the reactor during one hour (at room temperature). After carbonatization the product was dried at 200 °C, while the X-ray diffraction analysis found the presence of Mg-carbonates (hydromagnesite, dypingite, and giorgiosite) in addition to the non-reacting MgCl$_2$.6 H$_2$O.

The implementation of the indirect carbonatization according to equations 4-5 or 5-8 is economically and technologically extremely demanding and requires compliance with the strict requirements of the technical and material facilities, as well as with the protection of the environment.

6.4.1.2 Mineral sequestration of CO$_2$ in HO-2 sample material

For the detection and determination of the dependence of reactivity of magnesium component from the serpentine of the HO-2 sample from Hodkovce site the carbonatization tests were carried out with only mechanically modified grist (grit ground for three hours – Table 6.4) with gradual increase of carbon dioxide action upon the suspension (1, 3, 6, 12 and 24 hours). The aim was to create the new Mg-carbonate product in the high-pressure reactor under optimal CO$_2$ input pressure of 6 MPa and ambient temperature 22 °C with stirrer speed 300 rpm. After the process the suspension was divided by filtration into the solid phase (filter cake) and the liquid phase (filtrate), from which the new product containing Mg-carbonate was obtained by drying-crystallization. The results of the laboratory experiments of mineral sequestration of CO$_2$ are shown in Table 6.19.

Tab. 6.18 Sequestration of CO_2 in laboratory tests using chemically modified grit of the HO-2 sample at extraction temperature T=22 ºC and 100 ºC during 1, 2 and 3 hours and followed by carbonatization under the input CO_2 pressure of 6 MPa, duration of CO_2 exposure 1 hour.

Chem. compound	Input HO - 2	Filt. cake after extr. at **22 ºC**			Precipitated product after 1 h carbonatization		
		1 hour	**2 hours**	**3 hours**	**1 hour**	**2 hours**	**3 hours**
MgO	36.73	25.7	22.8	21.6	26.8	27.2	28.5
CaO	0.24	0.14	0.16	0.20	0.39	0.27	0.21
Fe_2O_3	8.04	4.63	4.37	4.01	7.7	8.8	8.53
Loss by ign.	13.44	20.5	23.9	21.0	32.3	37.9	38.2
CO_2	0.19	0.43	0.74	0.54	10.3	14.7	13.0

Chem. compound	Input HO - 2	Filt. cake after extr. at **100 ºC**			Precipitated product after 1 h carbonatization		
		1 hour	**2 hours**	**3 hours**	**1 hour**	**2 hours**	**3 hours**
MgO	36.73	19.6	14.1	11.0	41.3	42.4	43.4
CaO	0.24	0.13	0.14	0.14	1.32	1.43	1.17
Fe_2O_3	8.04	4.4	4.53	3.8	0.03	0.03	0.04
Loss by ign.	13.44	16.3	16.4	16.6	51.9	51.7	52.0
CO_2	0.19	0.21	0.08	0.18	30.7	31.1	30.3

Tab. 6.19 The increments values of the mass yields of precipitated products (%) depending on the time of CO_2 action upon mechanically activated HO-2 sample (ground for 3 hours) at the input CO_2 pressure of 6 MPa, stirrer speed 300 rpm and the ambient temperature 22 °C

Action time of CO_2 (hours)	Site Hodkovce **HO-2**	Mineral compounds in new product detected by X-ray diffraction analysis
1	+ 0.78%	hydromagnesite, brucite, AF
3	+ 0.92%	hydromagnesite, brucite, AF
6	+ 1.00%	hydromagnesite, brucite, AF
12	+ 1.22%	hydromagnesite, brucite, AF
24	+ 1.54%	hydromagnesite, brucite, AF

Note: AF – amorphous phase

The filter cake (non-reacted solid phase) and the new (precipitated) carbonate product of the filtrate were subjected after 24 hours to X-ray diffraction chemical analysis, and their results are given in Table 6.20.

The Table 6.20 shows that the proportion of Mg-component reacted with CO_2 leading to a creation of new product containing hydromagnesite. From the Table 6.19 it follows, however, that the increment in the mass yield of the new product with Mg-carbonate increased only slightly with the extension of CO_2 action, namely from the value of 0.78% (after 1 hour) to 1.54% (after 24 hours). This is due to the fact that the mechanical activation (grinding of the HO-2 sample for three hours on grit as referred to in Table 6.4) still did not release sufficiently Mg-component from the serpentine minerals for reaction with CO_2, as evidenced by the presence of a dominant crystallic lizardite in the filter cake.

From the pairs of values of the five experiments (Table 6.19) there was compiled equation of the mass yield increment of precipitated products vs the mechanically modified HO-2 sample exposed to carbon dioxide, at optimal input CO_2 pressure of 6 MPa. This dependence is visualised in Figure 6.6.

Tab. 6.20 Chemical and mineral composition of the precipitated product and the non-reacted residue after 24-hour carbonatization of the mechanically activated HO-2 sample (3 hours ground grit)

Compound	Product	% of compound content by weight				
		SiO_2	Fe_2O_3	MgO	CO_2	Ign. loss
chemical	**precipitated**	9.05	0.19	41.2	25.1	44.1
	filter cake	39.9	8.67	35.9	0.69	13.2
mineral	**precipitated**	hydromagnesite 66.7%; amorphous phase (+ brucite) 33.3%;				
	filter cake	lizardite 80.5; Fe oxides 8.7; hydromagnesite 1.8; amorphous Si phase 7.0; other minerals 2.0;				

The dependence of mass yield increment of the new precipitated carbonate product (y) upon the duration of CO_2 action (x), i.e. reactivity and binding of the Mg-component with the CO_2 within the crystal lattice of hydromagnesite in the grist of the sample HO-2 is characterised by the equation: $y = 0.229.Ln(x) + 0.7002$ with high correlation coefficient (r = 0.9497) at significance level 0.05

and for the selection range 5. According to this equation the increment in the mass yield of the new product in 6 days will be +1.84%, and, for example in 384 days + 2.79%, which testifies to the low speed of the reaction as a result of a insufficient release of the Mg-component from magnesium-rich minerals which underwent only mechanical modification with a duration of three hours.
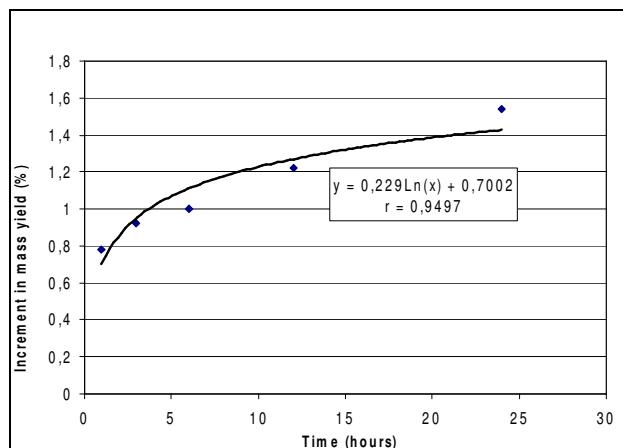
Fig. 6.6 Increments in the mass yield of precipitated products depending upon the time of CO_2 action upon mechanically activated HO-2 sample at CO_2 pressure of 6 MPa and ambient temperature 22 °C

In the case of fully amorphous phase of Mg-minerals (lizardite and olivine+pyroxene) by a sufficiently long milling of the sample HO-2 grit, with accompanying total destruction of the crystal lattice of the minerals and therefore full activation of the Mg-component for reaction with CO_2 the entire quantity of the Mg-component bound to the aforementioned minerals (MgO = 36.73%) reacts with CO_2 forming magnesite, or hydromagnesite (100% conversion), so **2,493 tonnes of the HO-2 sample are necessary to fix one tonne of CO_2, or 3,116 t of this sample/1 t CO_2.**

For the determination of the reactivity of magnesium component from the serpentine of the sample HO-2, activated both mechanically and thermally, with extension of the CO_2 action (1, 2, 3 hours) upon the grist suspension three tests were carried out. These three carbonatization experiments in the high-pressure reactor led to creation of a new product at optimal CO_2 input pressure of 6 MPa and ambient temperature 22 °C, with stirrer speed 300 rpm. After the above process the suspension was divided by filtration into filtrate and filter cake, from which new Mg-carbonate product was obtained by the drying-crystallization.

The results of the laboratory experiments of mineral sequestration of CO_2 are shown in Table 6.21.

Tab. 6.21 The increments values of the mass yields of precipitated products (%) depending on the time of CO_2 action upon mechanically and thermally activated HO-2 sample at the input CO_2 pressure of **6 MPa**, stirrer speed **300 rpm** and the ambient temperature **22 °C.**

Action time of CO_2 (hours)	Site Hodkovce **HO-2**	Mineral compounds in new product detected by X-ray diffraction analysis
1	+ 17.48%	hydromagnesite, amorphous phase, (AF)
2	+ 19.14%	hydromagnesite, AF
3	+ 24.36%	hydromagnesite, AF

Note: AF – amorphous phase

After 3 hours the filter cake (solid phase) and the new (precipitated) carbonate product from the filtrate were subjected to X-ray diffraction analysis and simplified chemical analyses; their results are presented in Table 6.22.

The Table 6.21 shows that the proportion of Mg-component reacted with CO_2 leading to a creation of the new product containing hydromagnesite. As it can be seen from the Table 6.22, the filter cake retains from the original input Mg-minerals only crystallic olivine, whereas the amorphous phase is only a relict part of the lizardite mineral; its crystal lattice was destructed by thermal modification of the grist due to the release of OH groups from the crystal lattice of this mineral.

The Table 6.21, shows, however, that with the gradually extended CO_2 action the increment in the mass yield of the new product containing Mg-carbonate increased from level 17.48% (after 1 hour) to 24.36% (3 hours), i.e. on nearly 7%. The increment in the mass yield of the precipitated Mg-carbonate product after 3 hour of carbonatization of mechanically activated grist was 0.92% (Table 6.19), in the case of mechanically and thermally activated grist 24.36%, which is 26.5 times more. This is due to the fact that the combined modification released sufficiently the Mg-component from lizardite, thus enabling for the reaction with CO_2. The proof for this is the absence of crystallic lizardite, or the presence of the amorphous phase and olivine in the filter cake.

From the pairs of values of three experiments (Table 6.21) the equation was compiled presenting the dependence between the increment in the mass yield of precipitated products vs duration of the mechanically and thermally modified HO-2 sample exposure to carbon dioxide action at optimal CO_2 input pressure of 6 MPa (Figure 6.7).
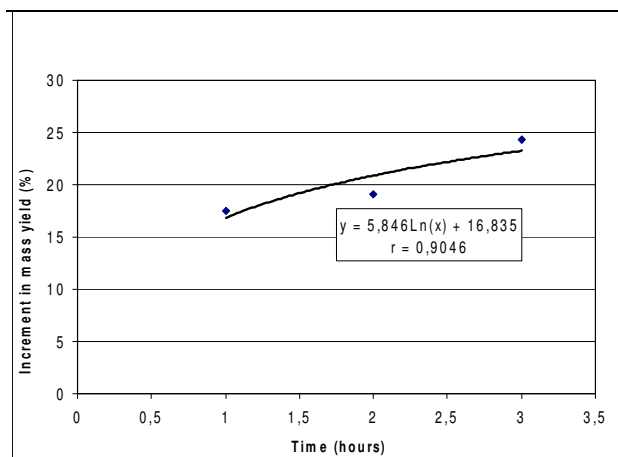
Fig. 6.7 Increments in the mass yield of precipitated products depending upon the time of CO_2 action upon mechanically and thermally activated HO-2 sample at CO_2 pressure of 6 MPa and ambient temperature 22 °C

The dependence between the increment in the mass yield of the new precipitated carbonate product and the duration of CO_2 action, i.e. reactivity and binding of the Mg-component with carbon dioxide in the hydromagne-

Tab. 6.22 Chemical and mineral composition of the precipitated product and the non-reacted residue after 3 hours carbonatization of mechanically and thermally activated HO-2 sample

Compound	Product	% of compound content by weight				
		Fe_2O_3	CaO	MgO	CO_2	Loss by ign.
chemical	**precipitated**	0.06	0.26	43.0	33.9	54.6
	filter cake	8.36	0.23	30.2	0.61	10.2
mineral	**precipitated**	Hydromagnesite 90%, amorphous phase 10.0%;				
	filter cake	amorphous phase, olivine;				

site crystal lattice for thermally modified grist of the HO-2 sample is characterised by the equation y = 5,846.Ln(x) + 16, with correlation coefficient r = 0.9046. According to this equation the increment in the mass yield of the new product in 6 days will equal + 45.89%, and in 384 days + 70.2%. This is a proof for continuous carbonatization as a result of a sufficient Mg-component release from the crystal lattice of entry magnesium minerals (mainly lizardite) due to thermally modified grist of the HO-2 sample, however, with gradual reduction of the reaction rate in time.

If the total quantity of Mg-component released from the serpentine mineral lizardite will react with CO_2 forming magnesite, or hydromagnesite (100% conversion), then according to MgO content of the precipitated product (Table 6.22), **3.88 tonnes of the HO-2 sample are needed per 1 tonne of CO_2.**

After three hours of carbonatization the new precipitated product containing hydromagnesite and with increment in the mass yield +24.36 % (Table 6.21), in which it is bound, according to the chemical analysis, 33.9% of CO_2 (Table 6.22), then, to capture one tonne of carbon dioxide 12.109 tonnes of the HO-2 sample are necessary and three hours of carbonatization.

By comparing the calculated values of the increments in the mass yields of the precipitated products in the 6 hour intervals (6, 12, 18, 24, 30, 36 and 42) according to the equation y = 5,846.Ln(x) + 16,835 it turns out that less than 1% difference in mass yield in two successive times of reaction occurred in the case of 36 and 42 hours, i.e. +0.91%. If the carbonatization takes 36 hours, according to the equation the mass yield increment of the new product containing hydromagnesite is +37.78%, which means in order to capture 1 tonne of CO_2, 7,030 tonnes of HO-2 material are needed in the 36-hour carbonatization.

6.4.1.3 Laboratory tests of carbonatization using HO-1 sample material

Similarly to the sample HO-2, the sample HO-1 also has considerable sequestration potential because it contains 36.06% of the Mg-component expressed as MgO. In order to accelerate the reaction of Mg-component with CO_2 the sample had to be fined down in order to increase specific surface (mechanical modification), in other words to release the Mg-component from the serpentine minerals lizardite and olivine+pyroxene by mechanical activation (crushing, grinding and sorting).

Mechanical modification of the sample

The sample HO-1 was collected a piece, the dimension of the largest piece of the sample was 150 mm. The sample was dried on open air, than crushed in three stages in the jaw crushers to a grain of approximately 1 mm, homogenized and quartered. The prepared grit was subjected to wet granulometric analysis (Table 6.23). The next step was the grit grinding for 3 hours (to increase the specific surface), and the Table 6.24 presents the granulometric analysis of the sample grist.

Tab. 6.23 Wet granulometric analysis of the sample HO-1

Granulometric class (mm)	Mass yield in %		
	class	total residue	undersize in total
+ 1.0	1.97	1.97	-
0.5-1.0	21.73	23.70	98.03
0.2-0.5	31.77	55.47	76.30
0.1-0.2	13.87	**69.34**	44.53
0.063-**0.1**	5.67	75.01	**30.66**
0.045-0.063	2.40	77.41	24.99
0.020-0.045	4.93	82.34	22.59
-0.020	17.66	-	17.66
In total	100.00	-	-

Tab. 6.24 Wet granulometric analysis of the sample HO-1 grist after 3 hours of grinding

Granulometric class (mm)	Mass yield in %		
	class	total residue	undersize in total
+0.2	0.25	0.25	-
0.1-0.2	12.99	**13.24**	99.75
0.063-**0.1**	16.80	30.04	**86.76**
0.045-0.063	8.58	38.62	69.96
0.020-0.045	19.55	58.17	61.38
-0.020	41.83	-	41.83
In total	100.00	-	-

The granulometric analyses of grit and grist were carried out by wet method, the mass yield of granulometric classes, the total residue on the sieves, and the undersize fraction are related to the dry state of the sample.

The Table 6.23 shows that in the grit of the entry sample HO-1 the class below 1 mm is represented by

98.03%, while the proportion of the class below 0.1 mm is low – 30.66 %. The content of the finest granulometric class (-0,02 mm) is also small (17.66%).

The grist after 3 hours of milling contained 86.76 % of the class below 0.1 mm (in the sample HO-2 it was 92.73%), while the share of the finest granulometric fraction (0,02 mm) was 41.83 % (in the sample HO-2 it was 46.32%), implying that the hardness of the sample HO-1 is in terms of grindability greater than that of the sample HO-2.

To demonstrate the creation of new Mg-products number of laboratory tests of carbonatization was carried out on mechanically and thermally modified HO-1 sample, in which, after carbonatization in the reactor, CO_2 was bound in the crystal lattice of nesquehonite (drying-crystallization at 50 °C), or hydromagnesite (drying-crystallization at 200 °C).

The proof tests of mineral sequestration of CO_2 were carried out with the HO-1 sample under the same conditions as with the HO-2 sample.

The best conclusive results with prepared Mg-carbonates were achieved at the CO_2 input pressure of 0.3 MPa and room temperature of the suspension for 1 hour carbonatization of the sample grit thermally activated. By drying at 50 °C a highly-pure new product precipitated out of the filtrate with the dominant nesquehonite.

The precipitated new product contained 96.9% nesquehonite; 1.4% calcite and 1.7% other oxides (Si, Al, ...). By thermal analysis, which is characterized by endothermic effects, it was found that the product in temperature range between 105-360 °C released two molecules of water with a consequent mass loss of 35.5% (39.05% in theory).

In the temperature range 360-460 °C the release of one molecule of water from the crystal lattice of nesquehonite occurred with a mass loss of 15.7%, while in the range 460-580 °C the destruction of the crystal lattice took place, with a mass loss of 15.0%, i.e. for a range of 360-580 °C the mass loss is 30.7 % (31.81% in theory). Above 580 °C the amorphous MgO crystallizes to periclase, between 580-1000 °C the mass loss is negligible – 1.5%. The mass total loss in the temperature interval of 105-1000 °C is therefore 67.7% (70.86% in theory).

As regards the quality of the carbonatization product obtained by drying the filtrate at 200 °C, the new product precipitated with a dominant content of hydromagnesite. The best results were achieved under the same conditions as for the HO-2 sample.

The precipitated new product contained 95.5% hydromagnesite; 2.4% calcite and 2.1% other oxides (Si, Al, ...). By thermal analysis, which is characterized by endothermic effects, it was found that the product exposed to 360 °C releases four molecules of water with a mass loss of 17.3% (22.24% in theory).

In the temperature range 360-460 °C the functional OH group was released from the crystal lattice of hydromagnesite with a mass loss of 22.1%, while in the range 460-580 °C the disintegration of the crystal lattice occur-

red, with the release of CO_2 and consequent mass loss of 12.3%, i.e. for a range of 360-580 °C the mass loss was 34.4% (theoretically 36.25%).

Above 580 °C threshold gradual crystallization of the amorphous MgO to periclase occurs, whereas the mass loss in the interval 580-1,000 °C is negligible - 2.2%. The total mass loss in the temperature interval of 105-1,000 °C is 53.9% (theoretically 58.49%).

Simulation of P-T-t conditions of the carbonatization process and testing of CO_2 storage options in the newly created carbonate products were carried out in two sets of experiments, in the laboratory high-pressure reactor. The experiments were aimed in tracing the impact of growing CO_2 input pressure upon the value of the increments in the mass yield of the new (precipitated) product containing Mg-carbonates, on the grit and grist of the sample HO-1 at room temperature (22 °C), within one hour of the CO_2 action and constant stirrer speed (150 rpm). The results are given in Tables 6.25 and 6.26.

Tab. 6.25 Laboratory tests of CO_2 sequestration at 22 ^{0}C, on sample HO-1 grit, the duration of exposure to CO_2 was 1 hour, stirrer speed 150 rpm and under different pressures of CO_2

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 0,66	hydromagnesite, AF, aragonite ?
4.0	+ 0,70	hydromagnesite, AF, aragonite ?
6.0	**+ 0,82**	hydromagnesite, AF, aragonite ?
8.0	+ 0,66	hydromagnesite, AF, aragonite ?
10.0	+ 0,74	hydromagnesite, AF, aragonite ?

Note: AF – amorphous phase

Tab. 6.26 Laboratory tests of CO_2 sequestration at **22 ^{o}C,** on sample HO-1 grist, the duration of exposure to CO_2 was 1 hour, stirrer speed 150 rpm and under different pressures of CO_2

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 0.86	hydromagnesite, AF, aragonite ?
4.0	+ 0.80	hydromagnesite, AF, aragonite ?
6.0	**+ 0.92**	hydromagnesite, AF, aragonite ?
8.0	+ 0.84	hydromagnesite, AF, aragonite ?
10.0	+ 0.90	hydromagnesite, AF, aragonite ?

Note: AF – amorphous phase

Tables 6.25 and 6.26 show that the value of the increment in the mass yield of the new products containing hydromagnesite, amorphous phase and aragonite(?) are very close: for the grit (0.66-0.82%) and for the grist

(0.80-0.92%). With regard to the above fact in view of the increment in the mass yield of the new product and hydromagnesite content in the precipitated product, the CO_2 initial pressure of 6 MPa was chosen as optimal.

Thermal modification of the sample

Further experiments were aimed in increasing the values of the mass yield of new products after thermal modification of grit samples (thermal activation at 650 °C during one hour), under gradually growing CO_2 input pressure and three-levels of the environment temperature (22, 40, and 60 °C), within one hour of the CO_2 action and constant stirrer speed (150 rpm). The results are shown in Tables, 6.27, 6.28 and 6.29.

The tables indicate that the value of the increment in the mass yield of the newly created products containing hydromagnesite and aragonite(?) at temperatures of 22, 40, 60 °C of the environment are ranging in the orders 7.10-9.56%; 6.96-10.54% and 6.96-9.06%, i.e. approximately in the same ranges. Raising the temperature of the environment didn't have any significant impact on the increment in the mass yield of the new products under all trial pressures. This was also the case when the CO_2 initial pressure 6 MPa was elected as optimal (due to a technical, time and economic difficulty to reach subcritic state of carbon dioxide) at room temperature. The increment in the mass yield of the new product in these conditions was +8.94%, i.e. approximately 10 times higher than that of the original grit (+0.82% - Table 6.25).

Tab. 6.27 Laboratory tests of CO_2 sequestration at T = 22 °C using thermally modified grit of the sample HO-1, the duration of CO_2 action 1 hour, stirring speed 150 rpm and different pressures of CO_2

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 7.10	Hydromagnesite, AF, aragonite ?
4.0	+ 8.02	hydromagnesite, AF, aragonite ?
6.0	+ 8.94	hydromagnesite, AF, aragonite ?
8.0	+ 9.56	hydromagnesite, AF, aragonite ?
10.0	+ 9.02	hydromagnesite, AF, aragonite ?

Note: AF – amorphous phase

By comparing the values in the Tables of 6.27, 6.28 and 6.29, it is obvious that the increment in the mass yield of a new Mg-carbonate product in the case of thermally modified grit is generally 8% higher on average when changing the CO_2 pressure than it was in the original grit. This can be explained by the destruction of crystal lattice (in particular of lizardite) exposed to heat of 650 °C, with consequent release of chemically bound water (OH) and activation of the Mg-component entering in the reaction with carbon dioxide.

Due to the fact that the thermally modified grit gave after carbonatization the increment in the mass yield of up to approx. 10% of the new product containing hydromagnesite (Tables 6.27, 6.28 and 6.29), a set of tests was implemented with thermally modified grist (Table 6.26 - ground for 3 hours) at systematically changing input pressures of CO_2 during the one hour exposure to CO_2, constant stirrer speed (150 rpm) and ambient temperature - the results are shown in Table 6.30.

Tab. 6.28 Laboratory tests of CO_2 sequestration at T = 40 °C using thermally modified grit of the sample HO-1, the duration of CO_2 action 1 hour, stirring speed 150 rpm and different pressures of CO_2

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 6.96	hydromagnesite, AF, aragonite ?
4.0	+ 9.02	hydromagnesite, AF, aragonite ?
6.0	+ 9.84	hydromagnesite, AF, aragonite ?
8.0	+ 10.54	hydromagnesite, AF, aragonite ?
10.0	+ 10.06	hydromagnesite, AF, aragonite ?

Note: AF – amorphous phase

Tab. 6.29 Laboratory tests of CO_2 sequestration at T = 60 °C using thermally modified grit of the sample HO-1, the duration of CO_2 action 1 hour, stirring speed 150 rpm and different pressures of CO_2

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 6.74	hydromagnesite, AF, aragonite ?
4.0	+ 8.14	hydromagnesite, AF, aragonite ?
6.0	+ 8.60	hydromagnesite, AF, aragonite ?
8.0	+ 9.06	hydromagnesite, AF, aragonite ?
10.0	+ 8.56	hydromagnesite, AF, aragonite ?

Note: AF – amorphous phase

From the Table 6.30 we can see that at growing CO_2 input pressure from 2 to 10 MPa during one-hour exposure to carbon dioxide, the increment in the mass yield of Mg-carbonate is increasing from 11.78% to 14.76%, i.e. as opposed to the highest value of the thermally modified grit (Table 6.28 - 10.54%) the mass yield increased on about 1.24 to 4.22%.

The reactivity of carbon dioxide with an activated Mg-component in the sample HO-1 is also affected by the intensity of sample suspension mixing, i.e. dynamic environmental conditions, and therefore in the implementation of other tests using the CO_2 sequestration grist (Table 6.24) and thermally modified grist at room temperature

Tab. 6.30 Laboratory tests of CO_2 sequestration at T = 22 °C using thermally modified grist of the sample HO-1, the duration of CO_2 action 1 hour, stirring speed 150 rpm and different pressures of CO_2

Initial CO_2 pressure (MPa)	Increment in the mass yield (%)	Minerals in new product
2.0	+ 11.78	hydromagnesite, AF, aragonite ?
4.0	+ 13.62	hydromagnesite, AF, aragonite ?
6.0	+ 13.56	hydromagnesite, AF, aragonite ?
8.0	+ 14.48	hydromagnesite, AF, aragonite ?
10.0	+ 14.76	hydromagnesite, AF, aragonite ?

Note: AF – amorphous phase

there was chosen optimal stirrer speed 300 rpm (as it was by the HO-2 sample).

Chemical modification, in particular, the extraction of the Mg-component out of the entry minerals - lizardite, olivine+pyroxene, using acids or hydroxides was the same as in the sample HO-2, while each of the three following indirect methods of carbonatization has its merits and demerits. General feature of the three mentioned chemical ways of extraction of suitable component with subsequent carbonatization is their economic, technical and environmental complexity.

6.4.1.4 Mineral sequestration of CO_2 in the HO-1 sample material

For the detection and determination of the dependence of reactivity of Mg-component from the serpentine minerals of the only mechanically modified sample HO-1 from Hodkovce (grit ground for three hours – Table 6.26) the experiments in the high-pressure reactor were carried out under the following conditions: extension of carbon dioxide action upon the grist suspension (1, 3, 6, 12 and 24 hours) resulting in the creation of a new Mg-carbonate product, at optimal CO_2 input pressure 6 MPa and ambient temperature (22 °C), with stirrer speed 300 rpm. After the carbonatization process the suspension was divided by filtration into solid phase (filter cake) and the liquid phase (filtrate), from which a new product containing Mg-carbonate was obtained by drying-crystallization. The results of the laboratory experiments of mineral sequestration of CO_2 are shown in Table 6.31.

After 24 hours, the filter cake (non-reacted solid phase) and the new (precipitated) carbonate product of the filtrate were subjected to X-ray diffraction analysis and simplified chemical analyses. The results are given in Table 6.32.

The Table 6.32 shows that the proportion of Mg-component got in the reaction with CO_2 leading to the emergence of a new product containing hydromagnesite. However, from the Table 6.31, it is obvious that the increment in the mass yield of the new product with Mg-

carbonate increased only slightly with CO_2 action duration - from the value of 0.78% (after 1 hour) to 1.58% (after 24 hours). This is due to the fact that via mechanical activation (grinding of the sample HO-1 for three hours on grain as referred to in Table 6.24) the Mg-component will still not be released sufficiently from the serpentine minerals for reaction with CO_2. This was attested by X-ray diffraction analysis, which detected presence of crystallic lizardite and olivine+pyroxene in the filter cake.

From the pairs of values of five experiments (Table 6.31) the equation was compiled showing dependence of the increment in the mass yield of precipitated products upon the time of carbon dioxide action on the mechanically modified sample HO-1, at the optimal CO_2 input pressure 6 MPa (Figure 6.8).

Tab. 6.31 The values of the increments in the mass yields of precipitated products (%) depending upon the time of CO_2 action on mechanically activated sample HO-1 (ground for 3 hours), at the input pressure of 6 MPa, stirrer speed 300 rpm and the ambient temperature 22 °C

Action time of CO_2 (hours)	Site Hodkovce **HO-1**	Mineral compounds in new product detected by X-ray diffraction analysis
1	+ 0.78%	hydromagnesite, AF, aragonite ?
3	+1.00%	hydromagnesite, AF, aragonite ?
6	+ 1.22%	hydromagnesite, AF, aragonite ?
12	+ 1.34%	hydromagnesite, AF, aragonite ?
24	+ 1.58%	hydromagnesite, AF, aragonite ?

Note: AF – amorphous phase

The dependence of the increment in the mass yield of the new precipitated carbonate product upon the time of CO_2 action, i.e. reactivity and binding of the Mg-component with the CO_2 in the crystal lattice of hydromagnesite in the grist of the sample HO-1 is characterised by the equation $y = 0.2489.Ln(x) + 0.7582$ with a high correlation coefficient (r = 0.9947) and the significance levels 0.01 and 0.05 with a range of selection 5. According to this equation the increment in the mass yield of the new precipitated product for 6 days is + 2.0%, for 384 days + 3.03%, which testifies to the low speed of the reaction as a result of a lack of released Mg-component from entry magnesium minerals of only mechanically modified grit, ground for three hours, and the equations for both samples from Hodkovce are very similar.

In the case of fully amorphous phase of Mg minerals (lizardite and olivine+pyroxene) by a sufficiently long milling of the sample HO-1, with accompanying total destruction of the crystal lattice of the minerals and therefore full activation of the Mg-component for reaction with CO_2. In this case the entire quantity of the Mg-component bound to the aforementioned minerals (MgO = 36,06%), magnesite

Tab. 6.32 Chemical and mineral composition of the precipitated product and the non-reacted residue after the 24-hour carbonatization of the mechanically activated sample HO-1 (3 hours ground grit)

Compound	Product	% of compound content by weight				
		SiO_2	Fe_2O_3	MgO	CO_2	Loss by ign.
chemical	**precipitated**	16.7	0,22	33,8	22,9	38,9
	filter cake	39.2	7,85	36,2	1,13	13,9
mineral	**precipitated**	hydromagnesite 60.8%; amorphous phase (+aragonite?) 39.2%;				
	filter cake	lizardite; maghemite; pyroxene+olivine;				
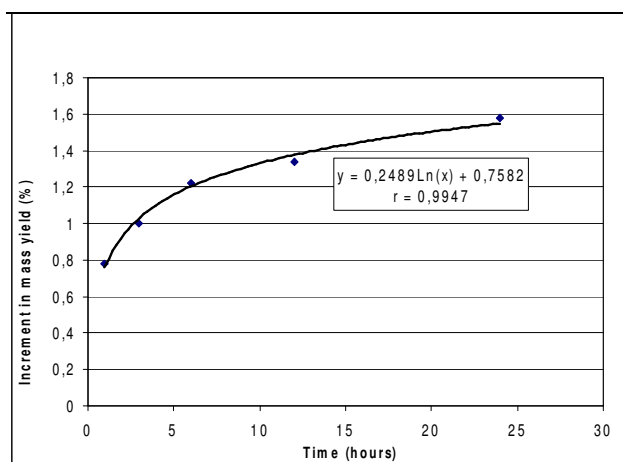
Fig. 6.8 Increments in the mass yield of precipitated products depending on the time of CO_2 action upon mechanically activated sample HO-1, at CO_2 pressure of 6 MPa and ambient temperature 22 °C

or hydromagnesite (100% conversion). **2.54 tonnes of the sample HO-1 are needed to capture 1 tonne of CO_2, or 3.174 tonnes of this sample/1 t CO_2.**

For the determination of the reactivity of Mg-component from the serpentine of the entry sample HO-1, which was activated both mechanically and thermally, with gradual increase of CO_2 action (1, 3, 6 hours) upon suspension of the modified grist three experimental tests of carbonatization were carried out in the high-pressure reactor resulting in the new precipitated product. The tests were realized at optimal CO_2 input pressure 6 MPa and ambient temperature (22 °C) with stirrer speed 300 rpm. The results of the laboratory experiments of mineral sequestration of CO_2 are shown in Table 6.33.

Tab. 6.33 The values of the increments in the mass yields of precipitated products (%) depending upon the time of CO_2 action on mechanically and thermally activated sample HO-1, at the input pressure of 6 MPa, stirrer speed 300 rpm and the ambient temperature 22 °C

Action time of CO_2 (hours)	Site Hodkovce **HO-1**	Mineral compounds in new product detected by X-ray diffraction analysis
1	+ 18.10%	hydromagnesite, AF
3	+ 23.74%	hydromagnesite, AF
6	+ 25.10%	hydromagnesite, AF

Note: AF – amorphous phase

By comparing the values in Tables 6.30 and 6.33 it is obvious that by increasing the stirrer speed from 150 to 300 rpm, at optimal CO_2 input pressure of 6 MPa acting for 1 hour, the increments in the mass yield of the new product containing hydromagnesite were 13.56% (150 rpm) and 18.1% (300 rpm).

After 6 hours the filter cake (solid phase) and the new (precipitated) carbonate product from the filtrate were subjected to X-ray diffraction analysis and simplified chemical analyses; their results are presented in Table 6.34.

The Table 6.33 shows that the proportion of Mg-component got into reacted with CO_2 resulting in creation of a new product containing hydromagnesite. As can be seen from the Table 6.34, the filter cake contains from the original input Mg minerals only crystallic olivine, whereas the amorphous phase is a relict of the serpentine mineral lizardite. Its crystal lattice was destructed by thermal modification of the grist due to escape of OH groups from the crystal lattice of this mineral.

From the Table 6.33 we can see t hat the increments in the mass yields of the new product containing Mg-carbonate of with gradually extended CO_2 action duration increased on 18.1% (after 1 hour) to 25.1% (after 6 hours), i.e. by 7%. Comparable increments in the mass yields of the Mg-carbonate product were achieved in the case of the sample HO-2 after 3 hours.

The increment in the mass yield of the precipitated carbonate product after 6 hour carbonatization of mechanically activated grist was 1.22% (Table 6.31). In the case of mechanically and thermally activated grist the increment was 25.1%, which is 20.6 times more. This is due to the fact that this combined modification of the sample HO-1 grist led in particular in lizardite to sufficient release of the Mg-component, which reacted with CO_2, which is testified by the absence of crystalline lizardite, or by the presence of the amorphous phase and olivine in the filter cake.

From the pairs of values of three experiments (Table 6.33) the equation was compiled showing dependence of the increment in the mass yield of precipitated products upon the time of carbon dioxide action on the mechanically and thermally modified sample HO-1, at the optimal CO_2 input pressure 6 MPa (Figure 6.9).

The dependence of the increment in the mass yield of the new precipitated carbonate product upon the time of CO_2 action, i.e. reactivity and binding of the Mg-component with the CO_2 in the crystal lattice of hydromagne-

Tab. 6.34 Chemical and mineral composition of the precipitated product and the non-reacted residue after 6 hour carbonatization of mechanically, and thermally activated sample HO-1

Compound	Product	% of compound content by weight				
		Fe_2O_3	CaO	MgO	CO_2	Loss by ign.
chemical	**precipitated**	0.04	0.98	43.02	34.7	54.1
	filter cake	8.78	0.72	31.30	1.44	10.4
mineral	**precipitated**	Hydromagnesite 92.2%; amorphous phase 7.8%;				
	filter cake	amorphous phase, olivine				

site in the grist of the sample HO-1 is characterised by the equation y = 4.0184.Ln(x) + 18.442 with a correlation coefficient (r = 0.9782) and the significance level 0.05 with a range of selection 3. According to this equation the increment in the mass yield of the new precipitated product for 6 days is +38.41% for 384 days +55.12%, which testifies to both fluent ongoing carbonatization in a period of more than 1 year as a result of sufficiently released Mg-component from the crystal lattice of the entry magnesium minerals (mainly lizardite) of thermally modified grist of the sample HO-1, but also to the gradual reduction of the reaction rate. The HO-2 sample material subjected to the same conditions of activation and carbonatization is a slightly more reactive.
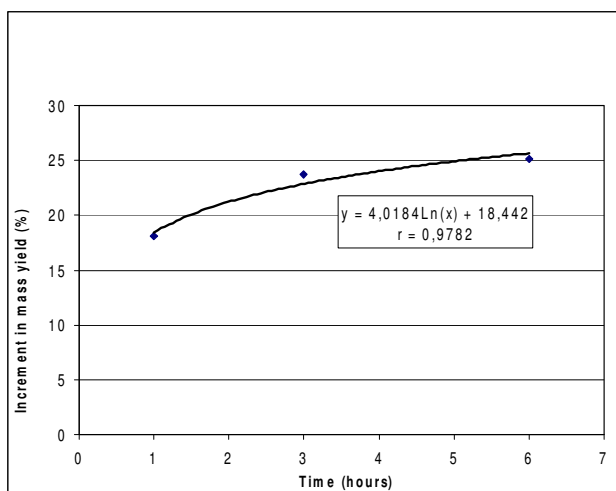
Fig. 6.9 Increments in the mass yield of precipitated products depending on the time of CO_2 action upon mechanically and thermally activated sample HO-1, at CO_2 pressure of 6 MPa and ambient temperature 22 °C

If the total quantity of Mg-component released from the serpentine mineral lizardite (by X-ray diffraction analysis the filter cake contains olivine) will react with CO_2 on hydromagnesite (100% conversion), then, in accord with the Table 6.34, **4.086 tonnes of the sample HO-1 are needed to capture one tonne of CO_2.**

After six hours of carbonatization the increment in the mass yield was +25.1%, the new product contained hydromagnesite (Figure 6.33), in which it was bound, according to the chemical analysis 34.7% of CO_2 (Table 6.34). Thus, 11,481 tonnes of the HO-1 material are necessary to capture one tonne of carbon dioxide/six hours carbonatization.

According to the equation y = 4.0184.Ln (x) + 18.442, the comparison of the calculated values of the increments in the mass yield of precipitated products in the 6 hour intervals (6, 12, 18, 24, 30 and 36) shows, that less than 1% difference in two successive times occurred in the case of 24 to 30 hours, i.e. +0.90%. For the 24 hours duration of the carbonatization reaction the increment in the mass yield of the new product containing hydromagnesite was +31.21%, which means that for the fixation of 1 tonne of CO_2 8.511 tonnes of the HO-1 material are needed during 24-hour of carbonatization.

6.5 Overall assessment of the achieved results

The laboratory research of the mineral sequestration of CO_2 in the form of a proof and trial tests of carbonatization was carried out on 18 pieces of technological samples from 14 geological sites; their chemical and mineralogical composition is referred to in Tables 6.1 and 6.2. The material of these samples contained minerals with MgO and CaO components; under specific conditions these components are suitable for CO_2 sequestration. In the reactions of these compounds with carbon dioxide in high-pressure reactor the carbon dioxide is fixed by binding to the crystal lattice of the newly emerging carbonate minerals.

The samples were divided into four groups according to the mineralogical composition (Table 6.2): serpentines (11 pcs), amphibolic-chloritic and talc serpentine (2 pcs), amphibolite (4 pcs) and basalt (1 pc).

The chemical composition of the samples (Table 6.1) indicates that the first group of samples contains serpentine minerals (especially lizardite and chrysotile) and olivine (+pyroxene), which bind in the crystal lattice Mg-component, whereas Ca-component in these samples is bound to calcite.

In the second group the carriers of the Mg-component are minerals talc and chlorite (sample from Beňuš site), out of a total content of MgO a part of the Mg-component is bound to the magnesite and dolomite, and the entire part of the Ca-component on the dolomite. In the Filipovo site sample the Mg-component is bound above all to the serpentine minerals and chlorite; the sample didn't contain carbonate minerals and calcium component was bound to amphibole.

In the amphibolite group the Mg-component is bound to chlorite and the Ca-component to amphibole, plagioclase and epidote with the exception of the sample from

the site Ostrá. In this sample almost entire amount of calcium is bound to calcite and only a tiny portion of the component to plagioclase. The basalt sample from the site Bulhary contains Mg-component bound to the pyroxene and olivine, and the Ca-component is bound to plagioclase and pyroxene.

By comparing the samples groups it is evident, that the highest sequestration capacity have serpentines, in which the contents of magnesium component expressed as MgO ranges from 34.75% to 39.73%, followed by amphibolic-chloritic and talc serpentines, in which the MgO-component content is in the range of 30.07-33.50%. The samples from the groups of amphibolite and basalt in terms of free contents of MgO and CaO (unbound to carbonates) have low sequestration potential.

The samples were subjected to mechanical modification (finening and grinding), and Table 6.35 presents grain-size distribution of grits and grists after three hours of grinding.

Subsequently sets of trial carbonatization experiments were carried out in the reactor on either mechanically, or mechanically-thermally (activation heat of 650 °C for one hour) modified samples in order to demonstrate the emergence of new products, the Mg-carbonates, in particular, in which the carbon dioxide was bound in the crystal lattice of nesquehonite (drying-crystallization at 50 °C) or of hydromagnesite (drying-crystallization at 200 °C), or Ca-carbonates (CO_2 fixation in the crystal lattice of calcite and aragonite, drying-crystallization at 200 °C) after carbonatization.

After the implementation of the carbonatization tests on samples the following experimental facts have been demonstrated:

– finer ground samples material is more suitable for the carbonatization;
– thermally modified sample material is more suitable;
– for the extraction of Mg-, or Ca-components from the entry material the temperature increasing and extending the duration of extraction is favoured;
– the efficiency of the extraction process is higher when using HCl than when using solution of NaOH;
– by drying the filtrate at 50 °C a new product precipitates with different content of nesquehonite depending upon the reaction conditions of carbonatization, or of extraction;
– by drying the filtrate at 200 °C a new product will precipitate with different content of hydromagnesite depending upon the reaction conditions of carbonatization, or of extraction;
– by drying the filtrate at 200 °C a new product will precipitate with different content calcite + aragonite depending upon the reaction conditions of carbonatization, or of extraction;
– dilution of suspension in water at carbonatization is manifested by lower crystallinity of hydromagnesite precipitated from the filtrate by drying at 200 °C;

– when using NaCl, or sodium hydroxide, in addition to the Mg-carbonates the precipitated product contained halite, Mg which can be removed by washing and decantation;
– at the extraction of Mg-component using HCl, in addition to the Mg-carbonates bischofite was present in the precipitated product (see chapter 7) and, the dominant were nesquehonite (drying at 50 °C), or hydromagnesite (drying 200 at °C) with a small content of amorphous substance and with the low contents of other Mg-carbonates (e.g. barringtonite, dypingite, giorgiosite, magnesite) documented by analysis using apparatus CAMECA SX 100, according to the reaction conditions.

The best conclusive results, when assessing the quality of prepared Mg-, or Ca-carbonates, were achieved at CO_2 input pressure of 0.3 MPa and ambient temperature, with duration of carbonatization for 1 hour, with thermally activated grist. From the filtrate dried at 50 °C new highly-pure product precipitated with nesquehonite content in the range 93.8-97.9% or hydromagnesite content in the range 90,6-97.5%, or with the dominant content of calcite+aragonite at 200 °C during drying of the filtrates.

The simulation of P-T-t conditions of the carbonatization process and testing of CO_2 storage options in the newly created carbonate products were realized in laboratory experiments in the high-pressure reactor. The experiments were aimed at tracing the impact of growing CO_2 initial pressure (in the range from 0.1 to 15.0 MPa) at room temperature (22 °C) and the increased one (between 40 and 60 °C), for various CO_2 action duration (from 1 to 24 hours) and different stirrer speeds (from 100 to 500 rpm) upon the values of increments in the mass yields of the new precipitated products with the content of Mg-, or Ca-carbonates from the samples either mechanically, mechanically-thermally or chemically modified.

The next step of the testing was determination of the reactivity of the Mg- or Ca-component from the entry material, either mechanically or mechanically-thermally activated, for various CO_2 action duration (1, 3, 6, 12 and 24 hours, or 1, 3 and 6 hours) upon the suspension of the grist, leading to formation of new product of Mg-, or Ca-carbonates. The carbonatization test were carried out in high-pressure reactor at optimal CO_2 input pressure 6 MPa and ambient temperature 22 °C, and optimum stirrer speed 300 rpm. After the process the suspension was divided by filtration into solid phase (filter cake) and liquid phase (filtrate), from which a new product crystallized by drying containing carbonates. On the basis of the results of the laboratory experiments of mineral sequestration of CO_2 the Tables 6.36 (mechanically activated samples) and 6.37 (mechanically-thermally activated samples) present the equations of the dependence between the increments in the mass yields of the new carbonate products and the duration of the exposure to carbon dioxide. In the Table 6.38 the increments in the mass yields of the precipitated products from mechanical-thermally activated

samples depending upon duration of CO_2 action are referred to; the values for the exposure times 1 and 6 hours were identified by experiments, and the values for 6 and 384 days were calculated using the equations from the Table 6.37.

In the Table 6.36 (mechanically activated samples) some of the values have attached symbols, which explain that for the samples **ŠE – 1, JK – 1, BA – 1, OS – 1 a BU – 1**:

* the entire quantity of CaO + MgO from the entry amorphous sample reacts forming $CaCO_3$ and $MgCO_3$;

** the total quantity of CaO + MgO, from the entry amorphous sample reacts forming $CaCO_3$ and hydromagnesite;

° only the "free" quantity from the entry amorphous sample reacts forming $CaCO_3$.

In the Table 6.37 (mechanically-thermally activated samples) the values in **the sixth column indicate**, that only MgO-component (value from chemical analysis) of serpentine minerals will react forming hydromagnesite, or in the samples **ŠE -1, JK-1, BA-1 and OS-1** only CaO-component (value from chemical analysis) will react forming $CaCO_3$. The values **in the seventh column** present, that according to the equation the calculated increment in the mass yield of the new carbonate product after given time is less than 1%, while the new product contains hydromagnesite, or for the samples **ŠE-1, JK-1, BA-1 and OS-1** $CaCO_3$. The values **in the eighth column** are calculated from the experiments with 6 hours duration with the emergence of the new product containing hydromagnesite or for the samples **ŠE-1, JK-1, BA-1 and OS-1** with the contents of $CaCO_3$, and the symbol **¹** attached to the HO-2 sample means duration in hours.

From the Table 6.36 it is obvious that the samples of only mechanically activated grit, ground for three hours, of the grain-size distribution referred to in the Table 6.35, the value of the increment in the mass yield of the new carbonate product is a function of the natural logarithm of the carbonatization duration. According to the values of the coefficient **k** in the equation the reactivity of all materials is low, whereas the rate of Mg-, or Ca-components reaction with CO_2 is slowing down with duration of CO_2 action. This is due to insufficient release of Mg-, or Ca-components from the entry mineral materials ground for three hours.

In general, for a group of serpentines samples the reactivity is slightly higher (k ~ 0.072 up to 0.249) than in the other samples (~ 0.051 up to 0.109), and after one hour of carbonatization at room temperature and CO_2 input pressure of 6 MPa for all samples only 0.57 to 1.88% increment in the mass yield of the new product containing Mg/Ca carbonates is achieved.

The Table 6.36 shows that in the case of fully amorphous Mg-, or Ca-minerals in the entry samples grit milled sufficiently long, there occur a total destruction of the crystal lattice of the minerals. Thus full activation of the Mg- and Ca-components for reaction with CO_2 is achieved, i.e. full amount of Mg- and Ca-components tied

to the minerals reacts with CO_2, forming $MgCO_3$ or $CaCO_3$, respectively (assumption of 100% conversion). 2.3 to 2.6 tonnes of a material from the serpentines samples are required to capture 1 tonne of CO_2, or 3.0 to 3.2 tonnes of material amphibolic-chloritic and talc serpentines samples per 1 tonne of CO_2, or from 5.6 to 14.4 tonnes of amphibolite and basalt samples material per 1 tonne of CO_2.

In the case of 100% conversion of Mg- or Ca-component on the hydromagnesite, or calcite+aragonite, 2.9 to 3.3 tonnes of serpentines material are required to capture 1 tonne of CO_2 or from 3.8 to 4.0 tonnes of chloritic-amphibolic and talc serpentines per 1 tonne of CO_2 or from 6.3 to 17.7 tonnes of amphibolite and basalt samples material per 1 tonne of CO_2.

From the Table 6.38 it is obvious that in mechanically-thermally activated samples (activation at 650 °C during one hour) the increment in the mass yield of the new carbonate product is also a function of natural logarithm of the carbonatization duration.

According to the values of the coefficient **k** in the equation the reactivity of the material samples is different. The highest reaction rate was achieved in serpentine samples designated **HO-1, HO-2 and RU-1**, in which the coefficient **k** ranged from 4.0 to 5.8 (HO-2), which is approx. 16 to 27 times the reaction rate against those samples only mechanically modified. In one hour carbonatization the new product with the increment in the mass yield ranged from 16.8 to nearly 22%. Paradoxically, the sample labelled **RU-2** from the same site (Rudník) had the reaction rate approximately 10 times lower (coefficient k = 0.5388 as opposed to 5.1263), but for one hour for both samples is the value of the increment in the mass yield of the new carbonate product similar (on average approximately 21.7%). Very good reactivity is manifested in the mechanically-thermally activated samples from the site Dobšiná (S-1) with a coefficient of 2.93 (grist) against coefficient 0.16 (ground grit); in this sample the highest value of the increment in the mass yield of the new product after one hour carbonatization was achieved up to 26.85% as opposed to the entry.

The reaction rate of the samples JA-1, KO-1/16 and BR-1 is expressed by the coefficient in the range 1.86-1.99, this means at least 10 x and higher, as in the samples only mechanically activated. A group of samples labelled KO-1/2, MI-1and FI-6 is characterised by the reactivity factor 0.82-0.98 (MI-1); in one hour the new carbonate product increment in the mass yield averages around 18.3% (KO-1/2 and MI-1) as compared to approximately 5 x less value (3.6% of sample FI-6).

In general, for the remaining group of mechanically-thermally activated samples (amphibolites and BE-1) the reactivity is low (~ 0.03 to 0,233) and comparable with the low coefficient of mechanically activated samples (~ 0.05 to 0.08), and after one hour of carbonatization at room temperature and CO_2 input pressure 6 MPa the increments in the mass yield of the new product containing Mg/Ca carbonates reached only from 0.29 to 4.3%.

Tab. 6.35 The contents of the granulometric classes (% by weight) in the samples grit and grist after 3 hours of grinding

Sample	Grit (mm)					Grist (mm)				
	+ 1.0	-1.0	+ 0.1	- 0.1	- 0.02	+ 1.0	-1.0	+ 0.1	-0.1	-0.02
HO-1	1.97	98.03	69.34	30.66	17.66	-	100.00	13.24	86.76	41.83
HO-2	2.13	97.87	73.96	26.04	17.47	-	100.00	7.27	92.73	46.32
RU-1	0.87	99.13	66.71	33.29	19.76	-	100.00	17.19	82.81	38.65
RU-2	2.67	97.33	73.26	26.74	13.70	-	100.00	20.30	79.70	39.97
JA-1	2.43	97.57	73.06	26.94	15.28	-	100.00	25.27	74.73	37.03
S-1	18.09	81.91	72.43	27.57	11.40	-	100.00	35.83	64.17	27.71
KO-1/2	76.46	23.54	92.93	7.07	-	0.68	99.32	72.07	27.93	11.12
KO-1/11	76.75	23.25	95.01	4.99	-	0.86	99.14	73.35	26.65	7.97
KO-1/16	75.16	24.84	90.81	9.19	-	1.32	98.68	70.29	29.71	10.28
BR-1	-	100.00	73.30	26.70	15.95	-	100.00	49.54	50.46	30.47
MI-1	-	100.00	59.44	40.56	23.82	-	100.00	41.70	58.30	32.50
FI-6	-	100.00	64.82	35.18	16.70	-	100.00	2.04	97.96	54.63
BE-1	-	100.00	70.24	29.76	15.34	-	100.00	5.07	94.93	52.54
ŠE-1	1.57	98.43	69.40	30.60	15.20	-	100.00	4.94	95.06	44.63
JK-1	-	100.00	76.96	23.04	10.17	-	100.00	40.05	59.95	30.03
BA-1	-	100.00	75.14	24.86	12.23	-	100.00	0.10	99.90	64.44
OS-1	-	100.00	75.07	24.93	14.60	-	100.00	0.40	99.60	69.13
BU-1	-	100.00	74.04	25.96	11.85	-	100.00	22.06	77.94	37.64

Tab. 6.36 The equations of the dependencies between the increments in the mass yields of the new carbonate product (y) of mechanically activated samples and the time of CO_2 action (x)

Sample	Equation	Correlation coefficient (r)	Significance level	Extent	Quantity (t) of amorphous material /1 t CO_2	
	$y = k . Ln (x) + q$				MgO to $MgCO_3$	MgO to hydromagn.
HO-1	$y = 0.2489 . Ln(x) + 0.7582$	0.9947	0.01; 0.05	5	2.540	3.174
HO-2	$y = 0.2290 . Ln(x) + 0.7002$	0.9497	0.05	5	2.493	3.116
RU-1	$y = 0.1872 . Ln(x) + 1.8838$	0.9414	0.05	5	2.635	3.294
RU-2	$y = 0.2188 . Ln(x) + 1.1097$	0.9881	0.01; 0.05	5	2.511	3.138
JA-1	$y = 0.1942 . Ln(x) + 1.5798$	0.9879	0.01; 0.05	5	2.527	3.159
S-1	$y = 0.1603 . Ln(x) + 1.6418$	0.9905	0.01; 0.05	5	2.538	3.171
KO-1/2	-	-	-	-	2.305	2.881
KO-1/11	-	-	-	-	2.370	2.962
KO-1/16	-	-	-	-	2.305	2.881
BR-1	$y = 0.0715 . Ln(x) + 1.8096$	0.9772	0.01; 0.05	5	2.482	3.102
MI-1	$y = 0.1122 . Ln(x) + 1.5201$	0.9881	0.01; 0.05	5	2.558	3.197
FI-6	$y = 0.1087 . Ln(x) + 0.5821$	0.9990	0.01; 0.05	5	3.046	3.806
BE-1	$y = 0.0514 . Ln(x) + 1.1161$	0.9899	0.01; 0.05	5	3.211	4.013
ŠE-1	$y = 0.0549 . Ln(x) + 0.8341$	0.8931	0.05	5	6.552*	7.376** (14.850 °)
JK-1	$y = 0.0811 . Ln(x) + 1.0453$	0.8729	0.05	5	6.675*	7.433** (13.612 °)
BA-1	-	-	-	-	7.816*	8.402** (12.007 °)
OS-1	-	-	-	-	14.361*	17.712** (265.111 °)
BU-1	$y = 0.0625 . Ln(x) + 0.5730$	0.9476	0.05	5	5.597*	6.284** (12.357 °)

The Table 6.37 in the seventh column presents the values of the quantities of thermally activated crushed material, and to the value the carbonatization duration is attached at the CO_2 input pressure of 6 MPa and ambient temperature. The values in the increments in the mass yield of the new carbonate product are less than 1%.

The Table 6.37 is amended on the Table 6.38, which presents the values of the increments in the mass yield of the new carbonate product activated mechanically-thermally for 1 and 6 hours (the results of laboratory experiments), and 6 and 384 days, respectively, calculated from the equations (Table 6.37), which were drawn up on the basis of the results of the experiments.

Tab. 6.37 The equations of the dependencies between the increments in the mass yields of the new carbonate product (s) from mechanically and thermally activated samples and the time of CO_2 action (x)

Sample	Equation	Correlation coeff. (r)	Significance level	Extent	Quantity (t) of mech. and therm act. rock /1 t CO_2		
	y = k . Ln (x) + q				MgO from serp.	Increment < 1%	CO_2/CHA/6 h.
HO-1	y = 4.0184 . Ln(x) + 18.4420	0.9782	0.05	3	4.086	8.511/24 hours	11.481
HO-2	y = 5.8460 . Ln(x) + 16.8350	0.9046	-	3	3.880	7.030/36 hours	12.109[1]
RU-1	y = 5.1263 . Ln(x) + 21.9540	0.9999	0.01; 0.05	3	5.069	6.743/30 hours	10.380
RU-2	y = 0.5388 . Ln(x) + 21.4010	0.9644	0.05	3	4.173	11.874/6 hours	12.907
JA-1	y = 1.9931 . Ln(x) + 13.2130	0.9978	0.05	3	4.346	14.616/12 hours	23.855
S-1	y = 2.9346 . Ln(x) + 26.8460	0.9892	0.05	3	3.599	7.518/18 hours	9.074
KO-1/2	y = 0.8591 . Ln(x) + 19.9790	1.0000	0.01; 0.05	3	4.520	12.343/6 hours	13.667
KO-1/11	-	-	-	-	-	-	-
KO-1/16	y = 1.9059 . Ln(x) + 16.1040	0.9237	-	3	4.343	12.745/12 hours	16.989
BR-1	y = 1.8597 . Ln(x) + 10.2020	0.9595	-	3	3.959	17.921/12 hours	26.385
MI-1	y = 0.9813 . Ln(x) + 16.6950	0.9658	0.05	3	3.717	14.397/6 hours	15.974
FI-6	y = 0.8204 . Ln(x) + 3.6029	0.9986	0.05	3	8.825	52.389/6 hours	83.333
BE-1	y = 0.0338 . Ln(x) + 4.3008	0.9982	0.05	3	7.641	57.985/6 hours	84.034
ŠE-1	y = 0.1418 . Ln(x) + 1.1300	0.9848	0.05	3	21.379	162.338/6 hours	248.880
JK-1	y = 0.0574 . Ln(x) + 1.0847	0.9793	0.05	3	15.215	190.985/6 hours	231.546
BA-1	y = 0.0760 . Ln(x) + 0.2934	0.9775	0.05	3	19.716	528.541/6 hours	961.538
OS-1	y = 0.2332 . Ln(x) + 1.6620	0.9262	-	3	297.371	109.266/6 hours	127.324
BU-1	-	-	-	-	-	-	-

The Table 6.38 shows that the most promising samples for carbonatization are the serpentines samples, and in particular the samples S-1 and RU-1, in which the increments in the mass yield of the new carbonate product were over 30% for 6 hours. Than followed the samples HO-1 and HO-2 (increment approx. 25-30%), samples RU-2, KO-1/2 and 1/16 (approx. 20-25%), JA-1 and MI-1 (approx. 15-20%) and BR-1 (increment approx. 10-15%). Other samples examined in view of the values of the increments in the mass yield are not promising for the fixation of CO_2.

6.6 Conclusions of the technological research

The most important output and the contribution of the technological research is identification and experimental demonstration of gaseous carbon dioxide sequestration in the geological materials from various sites across Slovakia in laboratory conditions. The CO_2 is permanently and stable fixed within the new carbonate products, containing, in particular, hydromagnesite, calcite and aragonite.

Comparing the groups of input samples has shown, that the samples of the first group-serpentines have clearly the highest sequestration potential, in which the content of magnesium component ranges from 34.75% to 39.73%. In second place are the samples of amphibolic-chloritic and talc serpentines, where the MgO content ranges from 30.07-33.50%. The samples from the groups of amphibolite and basalt reported in terms of the contents of MgO and free CaO (unbound to carbonates) have low sequestration potential.

Tab. 6.38 Increments in the mass yields of the new carbonate products of mechanically and thermally activated samples vs the time of CO_2 action

Sample	Increment in the mass yield of the new carbonate products (%)			
	From laboratory experiments		Calculated from equations in Table 6.37	
	1 hour	6 hours	6 days	384 days
HO-1	+ 18.10	+ 25.10	+ 38.41	+ 55.12
HO-2	+ 17.48	+ 24.36[1]	+ 45.89	+ 70.20
RU-1	+ 21.98	+ 31.18	+ 47.43	+ 68.75
RU-2	+ 21.46	+ 22.46	+ 24.08	+ 26.32
JA-1	+ 13.16	+ 16.70	+ 23.12	+ 31.41
S-1	+ 27.02	+ 32.38	+ 41.43	+ 53.64
KO-1/2	+ 19.98	+ 21.52	+ 24.25	+ 27.82
KO-1/11	-	-	-	-
KO-1/16	+ 16.42	+ 20.02	+ 25.58	+ 33.50
BR-1	+ 10.42	+ 13.88	+ 19.44	+ 27.18
MI-1	+ 16.80	+ 18.62	+ 21.57	+ 25.65
FI-6	+ 3.62	+ 5.10	+ 7.68	+ 11.09
BE-1	+ 4.30	+ 4.36	+ 4.47	+ 4.61
ŠE-1	+ 1.14	+ 1.40	+ 1.83	+ 2.42
JK-1	+ 1.08	+1.18	+ 1.37	+ 1.61
BA-1	+ 0.30	+ 0.44	+ 0.67	+ 0.99
OS-1	+ 1.70	+ 2.14	+ 2.82	+ 3.79
BU-1	-	-	-	-

According to the carbonatization results obtained the most perspective for CO_2 mineral sequestration is serpentine material with MgO-component content of about 37% tied mainly to serpentine minerals (chrysotile, lizardite), less to the minerals of olivine.

The best conclusive results, regarding the quality of prepared Mg-, or Ca-carbonates were achieved at CO_2 input pressure of 0.3 MPa, at carbonatization duration 1 hour at ambient temperature (22 °C) with the thermally activated samples (650 °C for 1 hour), in particular, from the serpentines group. By drying of the filtrate at 50 °C the new highly-pure product precipitated containing nesquehonite in the range 93.8-97.9% or hydromagnesite in the range 90.6-97.5%; at 200 °C drying of filtrates the dominant content was calcite+aragonite.

The simulation of P-T-t conditions of the carbonatization process and testing of CO_2 storage options in the newly created carbonate products with the subsequent finding and determination of magnesium, or calcium components reactivity of the input samples mechanically, or mechanically-thermally modified was carried out in the high-pressure stirring reactor PARR 4540. The optimum CO_2 input pressure was 6 MPa and ambient temperature was 22 °C. optimum stirrer speed 300 rpm. After the process the suspension was divided by filtration into the solid phase (filter cake) and the liquid phase (filtrate), from which the new product containing carbonates was obtained by drying-crystallization.

For the samples just mechanically, or both mechanical thermally activated the value of the increment in the mass yield of the new carbonate product (y) is the function of the natural logarithm of the carbonatization duration (x), i.e. $y = k.Ln (x) + q$, where q is the increment in the mass yield of the carbonate product after one hour.

According to the values of the coefficient **k** in each of the equations (Table 6.36) all the material just mechanically modified has low reactivity and reaction rate of Mg-, or Ca-components with CO_2 due insufficient release of Mg- or Ca-component from the entry minerals. In general, for the serpentines group of samples the reactivity is slightly higher (k ~ 0.072 to 0.249) than in the other samples (k ~ 0.051 to 0.109), and after one hour of carbonatization at room temperature and CO_2 input pressure 6 MPa for all samples the increment in the mass yield of the new product containing carbonates reached only up to +1.88%.

In the case of total amorphization of entry Mg- and Ca-minerals by sufficiently long grinding of the grit at estimated 100% conversion on $MgCO_3$, or $CaCO_3$, respectively, 2.3 to 2.6 tonnes of serpentines samples material are needed for fixation of 1 t of CO_2, from 3.0 to 3.2 tonnes of amphibolic-chloritic and talc serpentines samples material for fixation of 1 t of CO_2 or from 5.6 to 14.4 tonnes of amphibolite and basalt groups samples material for fixation of 1 t of CO_2 (Table 6.36).

In the case of 100% conversion of Mg-, or Ca-component on the hydromagnesite, or calcite+aragonite, 2.9 to 3.3 tonnes of serpentines samples material are required for fixation of 1 t of CO_2, from 3.8 to 4.0 of amphibolic-chloritic and talc serpentines samples material for 1 t of CO_2 or from 6.3 to 17.7 t of amphibolitee and basalt groups samples material for 1 t of CO_2 (Table 6.36).

For the mechanically-thermally activated samples the highest reaction rate was achieved in serpentines HO-1, HO-2 (Hodkovce) and RU-1, in which the coefficient **k** ranged 4.0 to 5.8, which is approx. 16 to 27 times the rate of a reaction of those samples only mechanically modified. Thus, in one hour of carbonatization new product is formed with a the increment in the mass yield from 16.8 to nearly 22%.

In terms of the input materials for the carbonatization an entry raw materials should be cheap and the site should be located in the vicinity of the processing plant, or a producer of CO_2 emissions. Welcome are the input materials with mineral components present, which have an exothermic reaction with CO_2, i.e. the heat that develops in the reaction can be utilised for carbonatization. For example, in the case of serpentine in the reaction with CO_2 a heat of 349 kJ.mol^{-1} CO_2 is released (exothermic reaction), in the case of forsterite in the carbonatization reaction 280 kJ. mol^{-1} heat of CO_2 is being released (Seifritz, 1990).

The results of the experimental laboratory research will, at least, partially contribute to the definition of the reactivity parameters affecting the conversion of gaseous CO_2 within geological materials into harmless solid mineral component (carbonates), which in the future may be the source for the design of technological schemes (implementation projects) in the model, pilot and operational scale for enterprises, which will necessarily have to reduce CO_2 emissions.

Finally, the exploitation of research results of CO_2 sequestration (disposal) by the way of carbonatization may contribute in the future to the four positive facts:

1) reduction in the quantities of CO_2 emitted into the atmosphere;

2) the reduction in the quantities and changing the properties of the stored waste materials;

3) saving the raw material resources by preparation of products which may be used in the industry;

4) the protection and creation of the environment as a whole.

7. Petrological study of CO_2 industrial emission bonding in minerals via artificial carbonatization of metaperidotite

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Abstract. The part extends an experimental base for possibility to store the carbon dioxide emission via artificial carbonatization of metaperidotite bodies located in the East Slovakia near Hodkovce village. Three types of hydrated mantle rocks, metaperidotite (metalherzolite), metawehrlite and metawebsterite were subjected to reaction with water and CO_2 and there from obtained suspensions were heated under different temperatures of 50 °C, 160 °C and 200 °C in the laboratory conditions. From the heated suspensions the acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite) and carbonates (calcite, dolomite, magnesite) were formed and confirmed by X-ray analyses. According to the mass balance calculations between the source silicate minerals (serpentine) and new carbonates-products, the mass from 1,070 kg to 1,429 kg of CO_2 can be sequestered in 1 m^3 of the source metaperidotite.

Key words: CO_2 disposal, artificial carbonatization, acid carbonates, carbonates, CO_2 storage capacity, metaperidotite, serpentinite

7.1. Introduction

The main sources of gases migrating to the atmosphere, including carbon dioxide that contributes to the greenhouse effect, derive from not only the high-emission technological processes, but also from other natural processes occurring on the surface and in the Earth's interior. Nowadays it is estimated that carbon dioxide concentration in the Earth's atmosphere has increased from 290 to 370 ppm during the last 150 years (Etherides et al. 1996; Drobek et al., 2008). The scientific evidence is now overwhelming: climate change presents very serious global risk and it demands an urgent global response. The method to remove the anthropogenous carbon dioxide is a sequestration, understood as capture or separation, transport and storage of the CO_2 emission in the deep geological structures. CO_2 sequestration methods are divided into:

– biological – intake through biosphere (photo-synthesis),

– physical – through storage in the ocean and deep geological structures; frequently proposed storage locations are exhausted hydrocarbons deposits (oil and natural gas), saline caverns or deep-lying brine water bearing strata, less frequently non-mined or not-balanced hard coal beds. This technology provides permanent prevention of carbon dioxide emission escaping to the atmosphere, while the monitoring of CO_2 leakages from the CO_2 stored deposit has to be continuous.

– chemical – by mineral carbonatization ("mineral sequestration"), consisting in binding CO_2 with minerals.

The mineral CO_2 sequestration is not so preferred in comparison to deposition in regional aquifers, or depleted hydrocarbon deposits. However it is concerned to be one of the approaches which can be helpful in the combat climate change (Schiller, 2006; Uibu, 2008).

Serpentinite has been proposed as an efficient reagent for CO_2 sequestration by reason that the highly magnesium serpentinite or forsteritic olivine favours the reaction to magnesite in hydrated mantle rocks (Deer et al., 1997). This reaction simultaneously allows deposition of the carbon dioxide in the serpentinite using its unnatural carbonatization (Herzog, 2002; Bochenczyk et al., 2007; Drobek et al, 2008). The final product of carbonatization is acid group of carbonates (nesquehonite, barringtonite, dypingite and hydromagnesite) as well as group of carbonates (calcite, dolomite, and magnesite) and silica. These minerals are stable without a negative effect on the environment (Lackner et al., 1995; Voormeij & Simandl, 2004; Dunsmore, 1992).

Serpentinite is formed by hydratation of olivine and enstatite at variable depths in the Earth's crust or mantle during regional metamorphism. Alternatively, it can be formed by water alternation at the surface in conformity with reactions 1, 2, and 3 (Johannes, 1968; Martin & Fyfe, 1970, Malakhov, 1971):

$$2Mg_2SiO_4 + 3H_2O = Mg_3Si_2O_5(OH)_4 + Mg(OH)_2 \qquad (1)$$
olivine $\qquad$ chrysotile $\qquad$ brucite

$$(Mg,Fe,Ni)_2SiO_4 + nH_2O = \text{serpentine group + magnetite}$$
olivine $\qquad\qquad\qquad$ + MgO + H_2 $\qquad$ (2)

$$Mg_2SiO_4 + MgSiO_3 + 2H_2O = Mg_3Si_2O_5(OH)_4 \qquad (3)$$
olivine   enstatite   chrysotile

According to the exchange reactions 4 and 5 the serpentine group (chrysotile) reacts with CO_2 to produce magnesite during its carbonatization in atmosphere conditions (Herzog, 2002, Drobek et al., 2008). However a process of artificial carbonatization uses NaCl and $NaHCO_3$ to produce intermediate product of $MgCl_2 + Mg(OH)_2$ and, consequently, the final carbonatization follows reactions:

$$1M\ NaCl + 0.64M\ NaHCO_3$$
$$Mg_3Si_2O_5(OH)_4 + 3CO_2 \qquad \rightarrow \qquad 3MgCO_3 + SiO_2 + H_2O \quad (4)$$
chrysotile $150^oC + 150$ atm CO_2 magnesite

$$Mg(OH)_2 + CO_2 = MgCO_3 \qquad\qquad (5)$$
brucite   magnesite
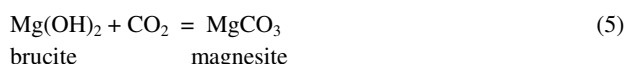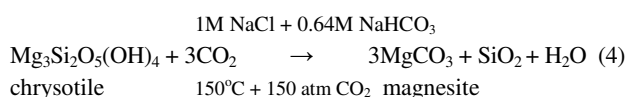
In term of reaction 4 is deducible, that for sequestration of 1 tonne of CO_2 is necessary to utilize a mass of 2.1 to 3.18 tonnes of serpentinite, in conformity with its density (Herzog, 2002). Both reactions (4 and 5), in agreement with numerous experimental works, irreversibly change the serpentine group of minerals (chrysotile, antigorite, lizardite) to carbonates. Serpentinite bodies are therefore efficient in CO_2 storage. Those bodies which were not influenced by natural CO_2 during metamorphism, or exhumation, are suitable for the artificial carbonatization purposes. Therefore a mineralogical and petrological study of the bodies is needed, because their results are crucial to select a suitable body in the mineral sequestration methodology.

There are several occurrences of partially or completely serpentinised metaperidotites bodies in the Slovak Republic. A targeted research for asbestos-lizardite occurrence was carried out at the sites Jaklovce, Sedlice, Dobšiná, Breznička - Kalinovo, Komárovce - Hodkovce, Rudník and Jasov in the past (Zlocha & Hovorka, 1971, Zlocha, 1980, Grecula et al., 1995). These bodies are almost completely serpentinised and accompanied with variable content of carbonate finds (Hovorka et al., 1985). It means that their evaluation for calculations of carbon dioxide sequestration requests detailed mineralogical and petrological study. However this is not the only criterion for usable serpentinite body, but its volume, depth, morphology and tectonic structure are certainly important as well (Fig. 1.1).

A dominant CO_2 producer in Slovakia is US STEEL Ltd. with annual production of more than 11 Mtons per year. The surrounding of this plant from the geological point of view is suitable for CO_2 storage by various methods. The area near the producer is the largest ultramafic body of metaperidotite, with extension about several km^3. The outcrop of metaperidotite is located near Hodkovce. In addition to the Komárovce – Hodkovce large body, there is located small metawebsterite body near Rudník and the metawehrlite body near Jasov, both having several 100 m^3 in size (Zlocha, 1980). Encouraging of body circumstances in the depth is confirmed by a high temperature gradient in Komárovce – Hodkovce metaperidotite body because the reactions 4 and 5, which transform serpentinite to carbonates, have an optimum temperature interval from 70 to 130 ^oC. A temperature of 59 ^oC has been measured in the depth below 1,500 m in the borehole KO-1 near Komárovce (Biela, 1978; Franko et al., 1995).

The aim of this study is to test the mantle rocks capability (metaperidotite, metawehrlite, metawebsterite), selected from the East Slovakian area for permanent carbon dioxide liquidation by artificial carbonatization. A consistent bonding of CO_2 in crystal lattice of carbonates is sustained and ecological solution for CO_2 mitigation purposes (Goldberg et al., 2000; Herzog, 2002; Kelemen & Matter, 2008).

7.2. Mineral composition of source mantle rocks

The serpentinized mantle-derived rocks were studied at the locality Hodkovce (samples HO-1, HO-2 and HO-3, metaperidotite). The minerals of serpentine group prevail over former magmatic mineral association (olivine and pyroxenes). Therefore it is possible to classify all the rocks studied as serpentinite.

Metaperidotite is formed by chrysotile (78 vol. % or 80%), olivine + enstatite + diopside (13%, or 10%), calcite and dolomite (1.3% or 0.4%), magnetite and hematite (8% or 9%). In the both samples the content of Cr-spinel is less than 0.5%. Moreover, it is possible to recognize hornblende, hornblende – pargasite, tremolite, Ni-sulphides and talc in accessory quantity.

7.3. Sample preparation and analytical conditions

Polished thin sections of source metaperidotite were studied under polarizing microscope. We have focused in the identification and volumetric evaluation of mineral phases. The composition of mineral association was measured by means of electron microprobe, Cameca SX-100, installed in the laboratory of the State Geological Institute of Dionýz Štúr, Bratislava. The microprobe was operated with accelerating voltage 15 KV, sample current 5-20 nA and the size of beam diameter varied from 5 to 20 μm in relation to the measured mineral. The counting time was 10 s and for fluorine 25 s. The following calibration standards were used: Ca-wollastonite, Mn-rhodonite, Na-albite, K-orthoclase and Cr-chromite., Ti-TiO_2, Al-Al_2O_3, Fe-fayalite, Mg-MgO and F-BaF_2. Detecting limit for individual elements was less than 0.05 wt.% with mistake 1 σ.

For the X-ray and chemical composition study, the rocks were firstly pulverized below 1 mm, homogenized and quartered. Homogeneous fraction was analyzed by X-ray diffractive inspection in the laboratory of the State Geological Institute of Dionýz Štúr, Košice and silicate analyses were obtained by differential thermogravimetric analysis (Tuček et al., 2009).

Experimental study has been conducted at this way dressed samples. The serpentinite was mixed with water and carbon dioxide according to the procedure used by
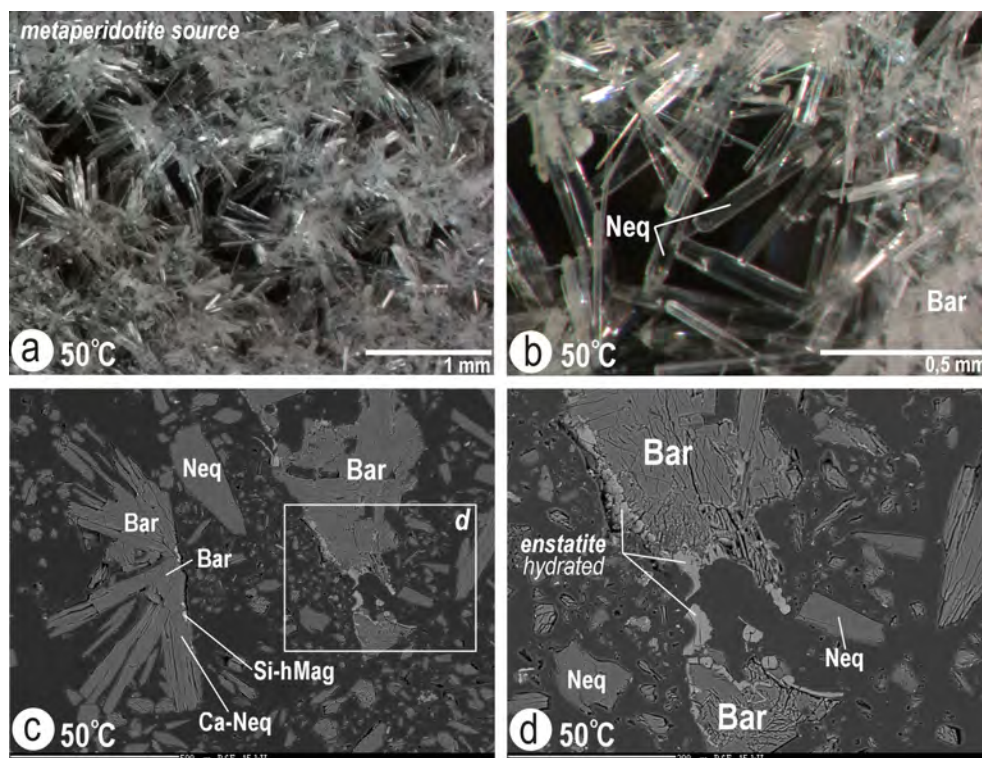
Fig. 7.1. Nesquehonite (Neq) and barringtonite (Bar) were formed during artificial carbonatization process at temperature 50 °C from the metaperidotite - serpentinite source. Sample HO-1, a) idiomorphic crystals of nesquehonite in binocular loupe, b) idiomorphic crystals of nesquehonite and barringtonite in binocular loupe, c) idiomorphic crystals of nesquehonite, barringtonite, Ca - nesquehonite (Ca-Neq) and Si hydromagnesite (Si-hMag). Back-scattered electron image, d) detail-c relic of hydrated enstatite and new barringtonite and nesquehonite. Back-scattered electron image.
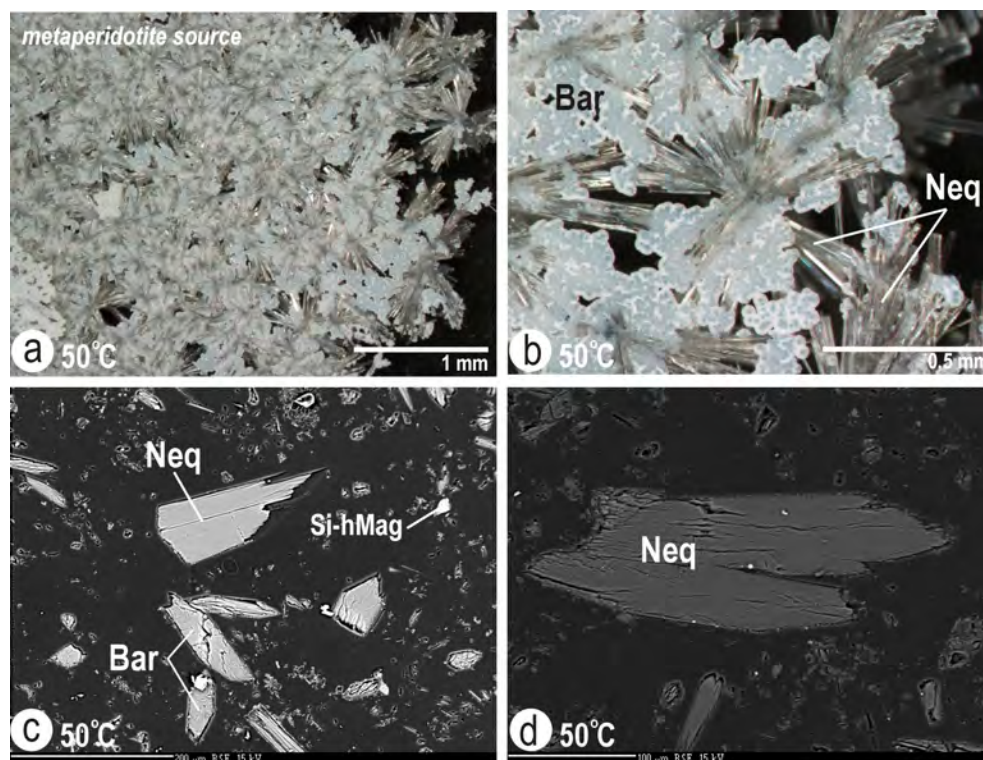
Fig. 7.2. Nesquehonite, (Neq), barringtonite (Bar) and hydromagnesite (hMag) formed by the artificial carbonatization process at temperature 50 °C from the metaperidotite - serpentinite source. Sample HO-2, a) nesquehonite and barringtonite in binocular loupe, b) nesquehonite and barringtonite in binocular loupe; c) nesquehonite, barringtonite, Ca and Si hydromagnesite (Si-hMag). Back-scattered electron image, d) nesquehonite in back-scattered electron image.

Tuček et al., (2009). Stable temperature 22 °C and CO_2 pressure from 0.1 to 0.3 MPa were maintained during controlled reaction from 5 to 20 hours. Leachates, with pH value about 8, became the source medium from which new products formed at temperatures 50 °C, 160 °C and 200 °C. The crystallization time was 4-24 hours. The new-formed and crystallized products were studied by optical methods and were analysed and controlled by the electron microprobe, by CHA (chemical silicate analysis), RTG (X-ray diffraction analysis), by DTA (differential thermic analysis) and by DTG (differential thermogravimetric analysis) where the almost end-member of acid carbonates and carbonates were found.

The photos of artificial carbonatization products were taken under binocular. The polished thin sections of reaction products were prepared and studied in optical microscope, as well. The chemical composition of new minerals was determined by spot electron microprobe analysis.

7.4. Minerals of artificial carbonatization formed at temperature 50 °C

A homogeneous idiomorphic nesquehonite or aggregations of nesquehonite and barringtonite up to size almost 1 mm were extracted from the suspension (serpentinite + CO_2 + H_2O) after reaction, filtration and crystallization from the filtrate (Fig 7.1 and 7.2). During the experiment the original source rock - metaperidotite was under constant temperature of 50 °C. A mixture of radially or omnidirectionally aligned nesquehonite was formed from the original metaperidotite. The nesquehonite and barringtonite were sporadically fibrillated by a hemisphere of hydromagnesite (Fig. 7.1c and 7.2c).
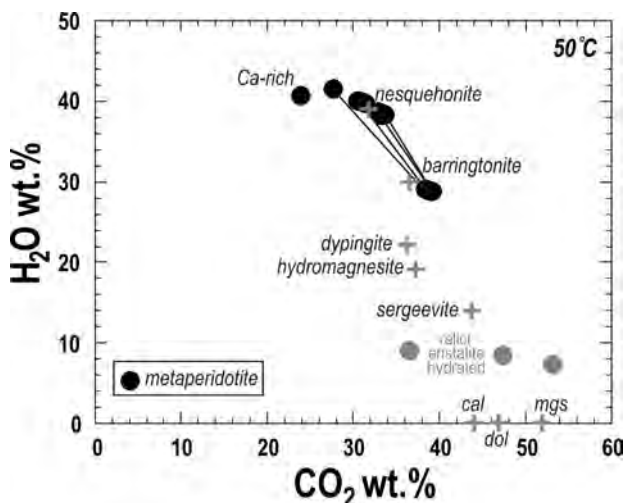
Fig. 7.3. Contents of H_2O and CO_2 in coexisting pair of nesquehonite - barringtonite (sample HO-1 and HO-2; metaperidotite source). These acid carbonates crystallized from the suspension (serpentinite + CO_2 + H_2O) during artificial carbonatization controlled by temperature 50 °C. Grey plus - contents of H_2O and CO_2 in end member minerals: cal - calcite, dol - dolomite, mag - magnesite. Grey circles - contents of H_2O and CO_2 in hydrated relic of enstatite.

Nesquehonite has almost identical values of X-ray diffraction profile and mineral lattice parameters as published in ASTM table values from the year 1974.

The chemical formula of nesquehonite is $Si_{0.001}Fe_{0.001}Cr_{0.001}Ca_{0.002}Mg_{0.995}$ $(HCO_3)(OH).2H_2O$; barringtonite $K_{0.001}Ca_{0.001}Mg_{0.999}CO_3.2H_2O$ and hydromagnesite $(K_{0.003}Na_{0.003}Si_{0.099}Al_{0.012}Fe_{0.005}Cr_{0.025}Ca_{0.083}Mg_{4.772})_5(CO_3)_4(OH)_2.4H_2O$ (Fig. 7.3, Tab. 7.1).

Table 7.1. Representative analyses of acid carbonates formed during artificial carbonatization by temperature 50 °C. Neq-nesquehonite, Bar-barringtonite.

Sample	HO-1	HO-1	HO-2	HO-1	HO-2
Mineral	Neq	CaNeq	Neq	Bar	Bar
Rock	peridotite	peridotite	peridotite	peridotite	peridotite
Temper.	50 °C	50 °C	50 °C	50 °C	50 °C
SiO_2	0.06	0.29	0.09	0	0.02
TiO_2	0	0	0	0	0
Al_2O_3	0	0.09	0	0	0
Cr_2O_3	0.06	0.08	0.03	0	0
FeO	0	0.03	0.07	0	0.02
MnO	0	0	0.02	0	0.01
MgO	28.33	17.63	29.59	32.48	32.18
CaO	0.03	17.11	0.04	0.04	0
Na_2O	0	0.06	0	0	0.04
K_2O	0	0.01	0	0.04	0
Cl	0	0.08	0	0	0
H_2O^*	38.20	40.67	39.98	29.08	28.83
Total	66.69	76.05	69.82	61.64	61.10
CO_2^*	33.31	23.95	30.18	38.36	38.90
Total *	100	100	100	100	100
O	4	4	4	3	3
Si	0.001	0.006	0.002	0	0
Al	0	0.002	0	0	0
Ti	0	0	0	0	0
Cr	0.001	0.001	0.001	0	0
Fe	0	0.001	0.001	0	0
Mg	0.995	0.580	0.992	0.999	0.998
Mn	0	0	0	0	0
Ca	0.001	0.405	0.001	0.001	0
Na	0	0.001	0	0	0.002
K	0	0	0	0.001	0
Total	0.998	0.998	0.997	1.001	1.000
CCl	0	0.006	0	0	0
OH	6	5.987	6	4	4

* calculated from chemical formula, $CO_2 = 100 - Total *$

Nesquehonite and coexisting barringtonite crystallized from the metaperidotite source after the reaction of serpentinite with a mix of the water and carbon dioxide according to the reaction 6. This reaction was derived from the relation between main responsive mineral in metaperidotite (chrysotile) and new originated minerals (nesquehonite, barringtonite). The reaction 6 precisely compares cations and anions balance in chemical formulas of minerals (Tab. 7.1). Low element contents were omitted in chemical formulas.

(metaperidotite source) $50^{\circ}C + 0.1 MPa\ CO_2$

$Mg_3Si_2O_5(OH)_4 + 3CO_2 + 6\ H_2O \quad \rightarrow \quad 2MgCO_3.3H_2O +$

serpentine group   nesquehonite

$+ MgCO_3.2H_2O + SiO_2$ (6)

   barringtonite

The formation of coexisting pair, nesquehonite – barringtonite, was generated at the temperature $50\,^{\circ}C$ on the expense of chrysotile after reactions 6. This pair is possible to clarify by reaction activity in the source metaperidotite (olivine, enstatite and diopside) from which the chrysotile was formed.

7.5 Minerals of artificial carbonatization formed at temperature 160 °C

A suspension of serpentine group minerals with CO_2 and H_2O was prepared from the source metaperidotite. This suspension was the source liquid from which after filtration and reaction under temperature regime 160 °C a spherical form of hydromagnesite and globular clumps mixture of dypingite and hydromagnesite have been formed and locally the size of crystals reached nearly 100 μm (Fig. 7.4). Original grains of Ca–Mg silicate (chrysotile, enstatite, diopside) were replaced by the mixture of dypingite, magnesite and dolomite. During the process of carbonatization rare allotriomorphic grains of dolomite and magnesite were formed reaching the size of 7 μm (Fig. 7.4c). Original diopside was in the course of carbonatization hydrated and replaced by hydromagnesite (Fig. 7.4d).

The chemical formula of hydromagnesite is: $(K_{0.002}$ $Na_{0.003}Si_{0.076}Fe_{0.002}Mn_{0.005}Cr_{0.007}Ca_{0.041}Mg_{4.861})_4(OH)_2.$ $4H_2O$; dypingite $(K_{0.006}Na_{0.016}Si_{0.021}Mn_{0.004}\ Fe_{0.002}Cr_{0.053}$ $Ca_{0.068}\ Mg_{4.832})_5(CO_3)_4(OH)_2.5H_2O$; dolomite $Ca_{0.39}Mg_{0.61}$ CO_3; magnesite $Ca_{0.01}Mg_{0.99}CO_3$ and calcite $Ca_{0.97}\ Mg_{0.03}$ CO_3 (Fig. 7.6. Tab. 7.2 and 7.3). In hydromagnesite the Cr_2O_3 content ranges from 0.11 wt. % to 1.85% and in dypingite from 1.02% to 1.54%. The presence of Cr_2O_3 in hydromagnesite and dypingite indicates a bond of Cr as the molecule of stichtite that formed the acid carbonates as well. The Cr_2O_3 content was not determined in magnesite, dolomite and calcite (Fig. 7.10).

The new assemblage of hydromagnesite, magnesite, dolomite and calcite is the final product of the reaction 7 where the serpentinite (chrysotile), diopside, and olivine reacted with H_2O and CO_2. This reaction was derived from the equation between the main consumed minerals and new formed minerals taking notice of exact relation between cations and anions balance in the chemical formulas of minerals (Tables 7.2 and 7.3). The small content of elements was neglected in the chemical formula.

(metaperidotite source) $160\,^{\circ}C$ and

$Mg_3SiO_2(OH)_4 + CaMgSi_2O_6 + Mg_2SiO_4 + 6CO_2 + 3H_2O \rightarrow$

serpentine group   diopside   olivine

$200\,^{\circ}C + 0.1 MPa\ CO_2$

$\rightarrow Mg_5(CO_3)_4(OH)_2.4H_2O + MgCO_3 + CaCO_3 + 5SiO_2$ (7)

    hydromagnesite   magnesite calcite
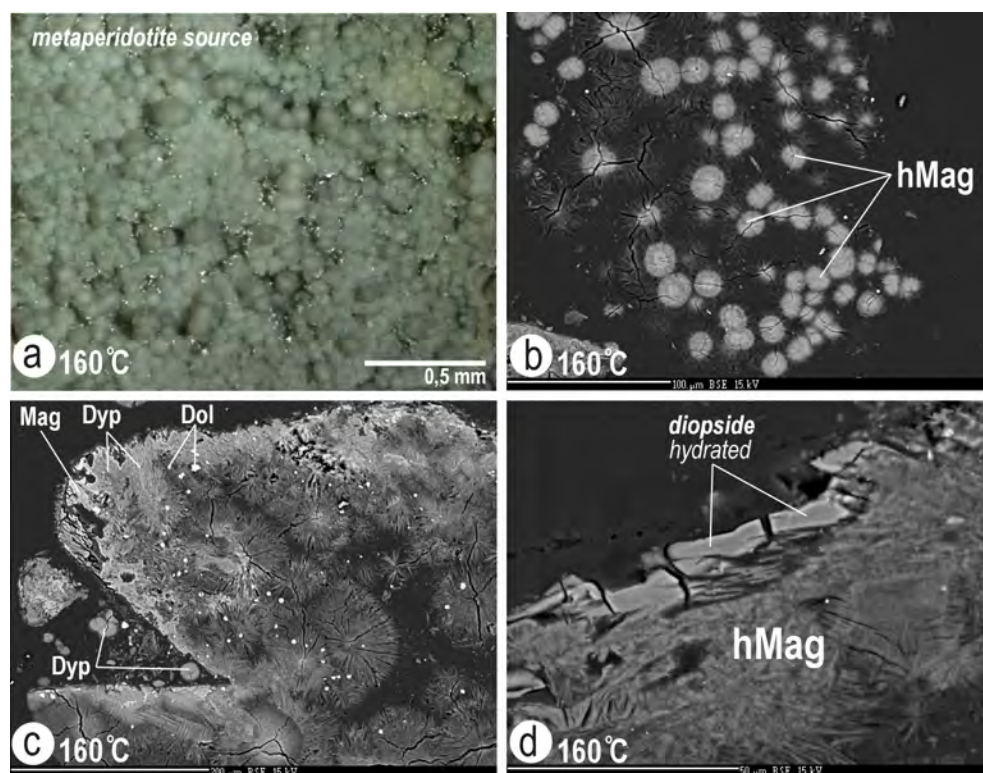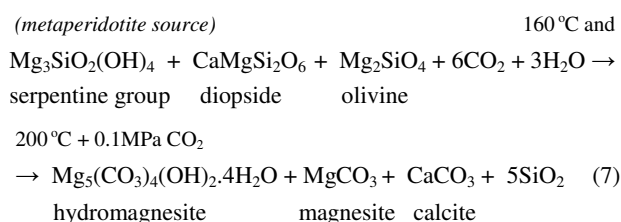
Fig. 7.4. Products of the artificial carbonatization were formed at temperature 160 °C from the metaperidotite - serpentinite source. Sample HO-2 a) hydromagnesite (hMag) in binocular loupe, b) hydromagnesite in back-scattered electron image, c) relic of enstatite replaced by magnesite (Mag), dypingite (Dyp) and dolomite (Dol). Back-scattered electron image, d) relic of hydrated diopside replaced by hydromagnesite. Back-scattered electron image.
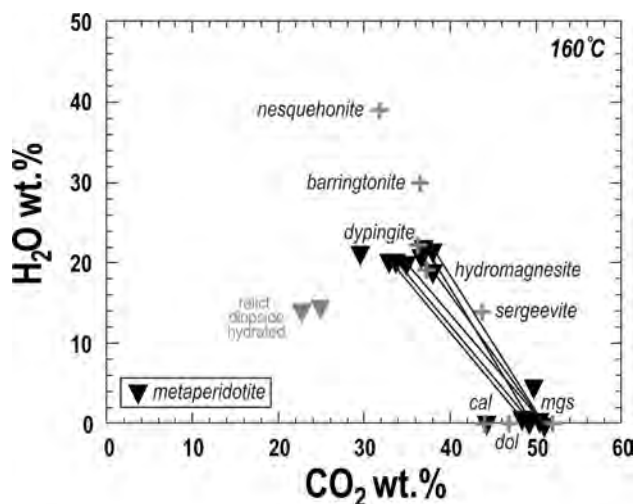
Fig. 7.5. Contents of H_2O and CO_2 in coexisting dypingite, hydromagnesite, calcite, dolomite and magnesite. Sample HO-2. These minerals were formed from the suspension (serpentinite + CO_2 + H_2O) during artificial carbonatization at temperature $160\,^oC$ and from the metaperidotite source. Grey plus - contents of H_2O and CO_2 in end member minerals: cal - calcite, dol - dolomite, mag - magnesite. Grey reverse triangle - content of H_2O and CO_2 in hydrated relic of diopside.

7.6 Minerals of artificial carbonatization formed at temperature 200 °C

Analogically to previous case, also in this experiment was used the temperature at 200 °C. The acid carbonate of the spherical form and the irregular aggregates of magnesite, hydromagnesite and Ca magnesite crystallized

Table 7.2. Representative analyses of acid carbonates formed during artificial carbonatization under temperatures 160 and 200 °C. Neq-nesquehonite, Bar - barringtonite, Dyp - dypingite, Ser - sergeevite, hMag - hydromagnesite.

Sample	HO-2	HO-2	HO-2	HO-1	HO-2	HO-2	HO-2	HO-2
Mineral	Dyp	hMag	hMag	Dyp	Ser	hMag	Neq	Bar
Rock	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite
Temper.	160°C	160°C	160°C	200°C	200°C	200°C	200°C	200°C
SiO_2	0.25	0.95	0.97	1.63	0.34	0.88	0.56	0.64
TiO_2	0	0	0	0	0	0	0	0
Al_2O_3	0	0.01	0	0.01	0.02	0.02	0.02	0.01
Cr_2O_3	1.02	1.80	0.11	0.13	0.02	0.18	0.10	0.03
FeO	0.03	0	0.05	0.03	0.34	0.06	0.01	0
MnO	0.06	0.03	0.07	0.01	0	0	0	0
MgO	38.57	43.14	41.36	34.54	20.19	43.28	28.16	34.73
CaO	0.57	0.76	0.48	1.39	19.27	0.61	0.39	0.53
Na_2O	0.10	0.16	0.02	0.04	0.01	0.02	0.02	0.04
K_2O	0.06	0.10	0.02	0.01	0	0	0.01	0.02
Cl	0.10	0.27	0.26	0.05	0.13	0.26	0.11	0.10
H_2O*	21.22	19.89	18.67	19.23	11.73	19.46	38.51	31.60
Total	61.98	67.11	62.01	57.07	52.05	64.77	67.89	67.70
CO_2*	38.02	32.89	37.99	42.93	47.05	35.23	32.11	32.30
Total *	100	100	100	100	100	100	100	100
O	11	10	10	11	23	10	4	3
Si	0.021	0.07	0.076	0.149	0.086	0.066	0.013	0.012
Al	0	0.01	0	0.001	0.006	0.002	0.001	0
Ti	0	0	0	0	0	0	0	0
Cr	0.068	0.105	0.007	0.009	0.004	0.011	0.002	0
Fe	0.002	0	0.003	0.002	0.072	0.004	0	0
Mg	4.832	4.729	4.861	4.694	7.607	4.874	0.975	0.976
Mn	0.004	0.002	0.005	0.001	0	0	0	0
Ca	0.051	0.060	0.041	0.136	5.218	0.049	0.010	0.011
Na	0.016	0.023	0.003	0.007	0	0.003	0.001	0.001
K	0.006	0.009	0.002	0.001	0.003	0	0	0
Total	5.000	4.999	4.998	5.000	12.996	5.009	1.002	1.000
CCl	0.028	0.067	0.070	0.015	0.111	0.067	0.009	0.006
OH	11.896	9.756	9.815	11.692	19.774	9.807	5.966	3.972

* calculated from chemical formula $CO_2 * = 100 - Total *$
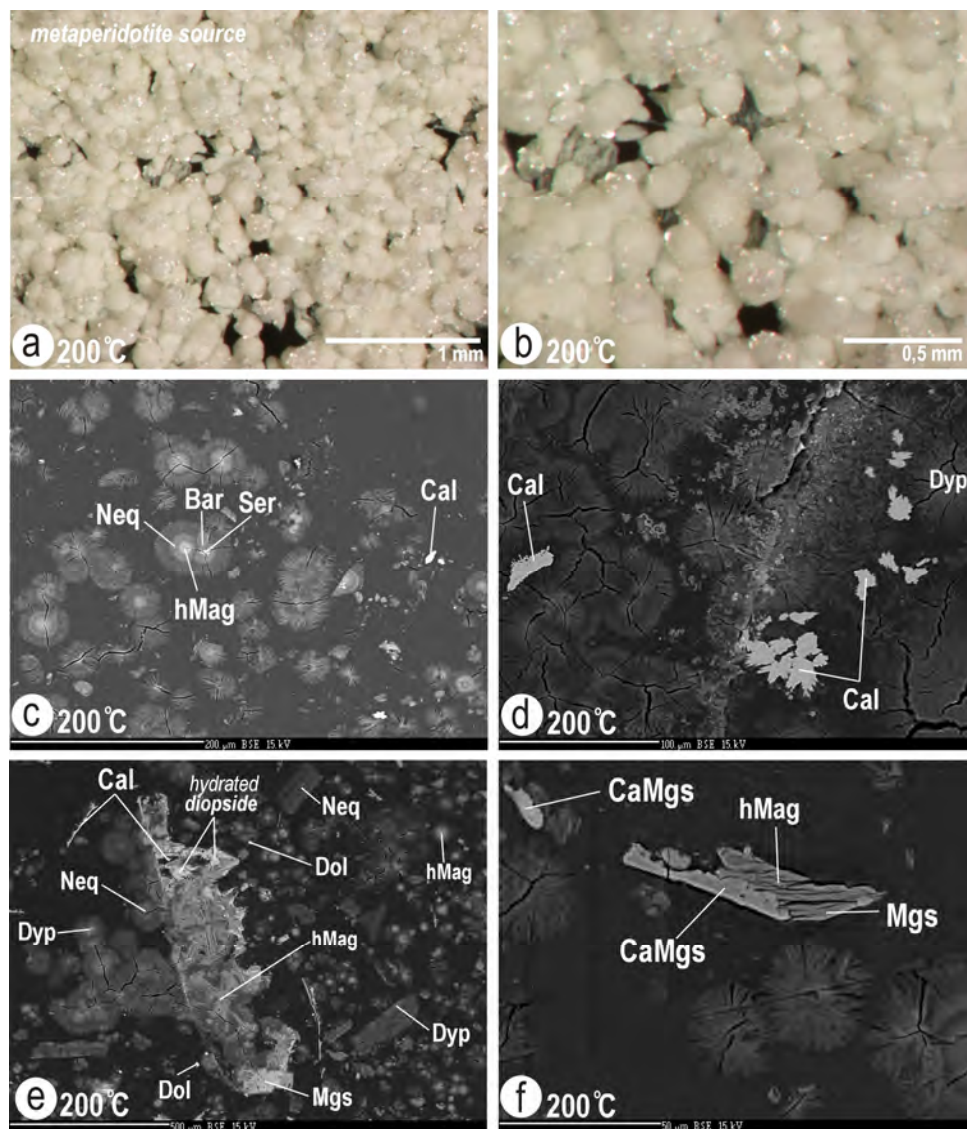
Fig. 7.6. Products of artificial carbonatization were formed at temperature 200 °C from the metaperidotite - serpentinite source. Sample HO-2, a) and b) spherical form of hydromagnesite (hMag), nesquehonite (Neq), barringtonite (Bar), sergeevite (Ser) and dypingite (Dyp) in binocular loupe, c) zonal grains of hydromagnesite (core), sergeevite (core), nesquehonite (rim), barringtonite (rim) and calcite (Cal). Back-scattered electron image, d) calcite and dypingite relation in back-scattered electron image, e) diopside replaced by calcite, by hydromagnesite, by dolomite (Dol) and magnesite (Mgs). Initial chrysotile (serpentine) was replaced by nesquehonite, hydromagnesite and dypingite. Back-scattered electron image, f) hydromagnesite, Ca magnesite (CaMgs) and magnesite in back-scattered electron image.
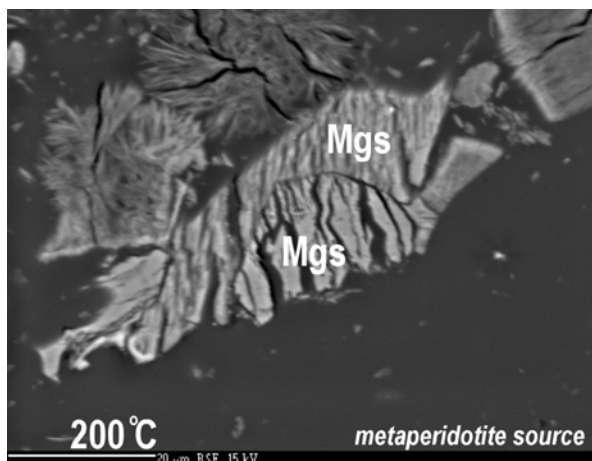
Fig. 7.7. Product of artificial carbonation was formed from metaperidotite source at the temperature of 200 °C. Sample HO-3; magnesite (Mgs) in back-scattered electron image.

Table 7.3. Representative analyses of carbonates formed during artificial carbonatization. Cal - calcite, Dol - dolomite, Mag - magnesite.

Sample	HO-2	HO-2	HO-2	HO-2	HO-2	RU-2	HO-2	HO-2	HO-2
Mineral	Cal	Dol	CaMag	Mag	Cal	Cal	Dol	CaMag	Mag
Rock	peridotite	peridotite	peridotite	peridotite	peridotite	websterite	peridotite	peridotite	peridotite
Temper.	160 °C	160 °C	160 °C	160 °C	200 °C	200 °C	200°C	200 °C	200 °C
FeO	0	0	0.02	0	0	0.01	0.04	0	0
MnO	0.03	0	0	0.03	0.11	0.02	0	0.01	0.10
MgO	0.85	27.03	39.42	46.70	1.40	1.72	27.58	40.73	47.59
CaO	55.45	24.12	10.08	0.87	54.49	53.76	23.10	7.34	0.28
CO_2^*	44.45	48.46	50.96	51.69	44.36	44.10	48.28	50.26	52.24
Total	100.78	99.61	100.48	99.29	100.36	99.61	99.00	98.34	100.21
O	3	6	3	3	3	3	6	3	3
Fe	0	0	0	0	0	0	0.002	0	0
Mn	0	0	0	0	0.002	0	0	0	0.001
Mg	0.021	1.218	0.845	0.987	0.034	0.043	1.248	0.885	0.995
Ca	0.979	0.782	0.155	0.013	0.964	0.957	0.750	0.115	0.004
Total	1.000	2.000	1.000	1.000	1.000	1.000	2.000	1.000	1.000

* calculated from chemical formula.

according to the reaction 7 from the source metaperidotite (Figs. 7.6 and 7.7). The spherical grains are zoned. The core form hydromagnesite, dypingite and/or sergeevite and the rim parts of rounded grains are formed by nesquehonite and/or barringtonite (Figs. 7.6c and 7.6e).

Hydromagnesite has almost identical values of X-ray diffraction profile and mineral lattice parameters as published in ASTM table values from the year 1974.

The chemical formula of nesquehonite is: $Si_{0.013} Cr_{0.002} Ca_{0.010} Mg_{0.975}(HCO_3).(OH).2H_2O$; barringtonite $Na_{0.001} Ca_{0.011}Si_{0.011}Mg_{0.976}CO_3.2H_2O$; dypingite $(K_{0.002}Na_{0.042} Si_{0.004}Mn_{0.002}Cr_{0.007}Ca_{0.033}Mg_{4.909})_5(CO_3)_4(OH)_2.5H_2O$; hydromagnesite $(K_{0.002}Si_{0.001}Mn_{0.001}Ca_{0.007}Mg_{4.989})_5 (CO_3)_4 (OH)_2.4H_2O$; sergeevite $(K_{0.006}Na_{0.013}Si_{0.458}Mn_{0.006} Cr_{0.025} Al_{0.003}Fe_{0.006}Ca_{1.845}Mg_{10.645})_{13}(CO_3)_9(HCO_3)_4(OH)_4.6H_2O$; calcite $Mg_{0.03}Ca_{0.97}CO_3$; dolomite $Mg_{0.62}Ca_{0.38}CO_3$; Ca magnesite $Mg_{0.89}Ca_{0.12}CO_3$ and magnesite $MgCO_3$ (Figs. 7.9 and 7.10, Tables 7.2 and 7.3).

During artificial carbonatization controlled at the temperature 200 °C the new coexisting assemblage, hydromagnesite, magnesite, calcite and dolomite was formed from the metaperidotite source (Figs. 7.6 and 7.7). The same assemblage is the result of serpentine group and olivine reaction with the water and carbon dioxide which was formed at the temperature 160 °C according to the reaction 7.

7.7. Discussion

The reactions 6 and 7 have been evaluated by mass balance calculations based on the relation between the source rocks of mantle and their respondent minerals (serpentine group, olivine, enstatite, diopside) and CO_2 + H_2O composition as well as according to new formed
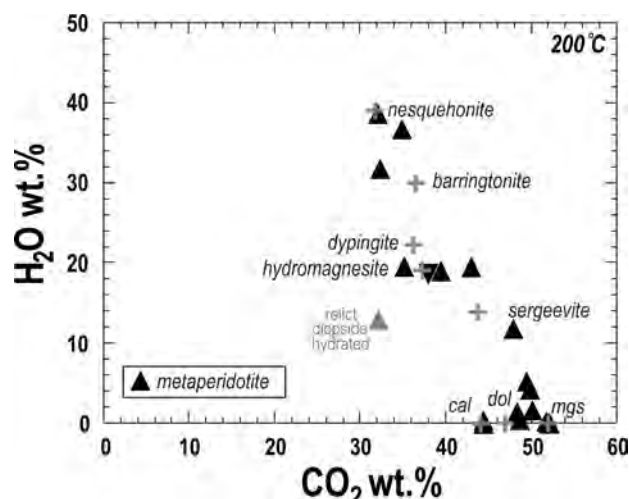
Fig. 7.8. Contents of H_2O and CO_2 in coexisting acid carbonates: nesquehonite, barringtonite, dypingite, hydromagnesite, sergeevite and carbonates: calcite, dolomite and magnesite. These minerals were formed from the suspension (serpentinite + CO_2 + H_2O) during artificial carbonatization at temperature 200 °C and from the metaperidotite source (sample HO-2 and HO-3). Grey plus - H_2O and CO_2 contents in end member minerals: cal - calcite, dol - dolomite, mgs - magnesite. Grey triangle – H_2O and CO_2 content in hydrated diopside.

acid carbonates and carbonates. These reactions represent the artificial carbonatization process, which can take place under various temperature conditions. A mass of carbon dioxide (kg) was calculated according to the mass balance of these reactions. Consequently, it allows to asses the mass of CO_2 consumed in 1 m³ of metaperidotite during artificial carbonatization process. In the course of reaction 6 controlled by temperature 50 °C is possible to consume 1429 kg of CO_2 in 1 m³ of metaperidotite, pro-
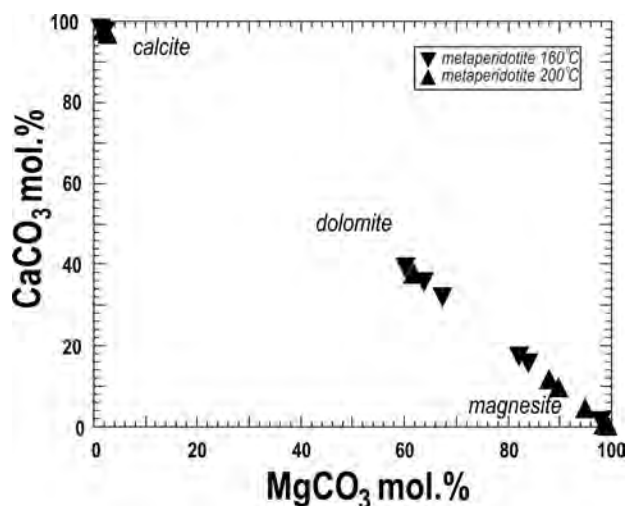
Fig. 7.9. Contents of CaCO₃ and MgCO₃ in carbonates. These minerals crystallized at the expense of silicates in metaperidotite.
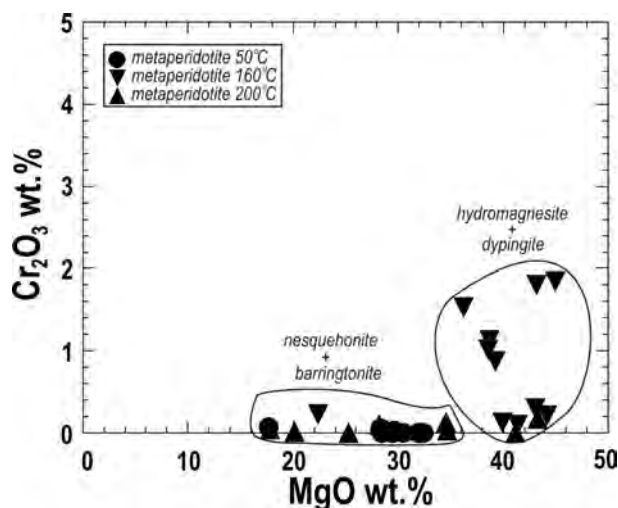
Fig. 7.10. Contents of Cr₂O₃ and MgO in nesquehonite, barringtonite, dypingite and hydromagnesite. Cr₂O₃ indicates presence of stichtite molecule Mg₆Cr₂(OH)₁₆(CO₃).4(H₂O) in these minerals.

vided the volume density of metaperidotite is 3.0 kg.m^{-3}. The capability of rock decreases to 1,224 kg of sequestered CO_2 in the case of lower volume density 2.57 kg.m^{-3} that is the value typical for serpentinite (Fig. 7.11).

The peridotite carbonatization process in conformity with the reaction 7 at temperature 160 $^{\circ}$C as well as 200 $^{\circ}$C consumes 1,249 kg of CO_2, alternatively, 1,070 kg of CO_2 in 1 m^3 of rock in dependence on minimum, or maximum substance of serpentine group in metaperidotite. The results obtained from our investigation are in a very good agreement with comparative investigation and calculation (Herzog, 2002).

In comparison to ideal weight of CO_2 eliminated in 1 m^3 of metaperidotite the consumed mass of carbon dioxide ranges from 1,070 kg to 1,429 kg and does not depend neither on temperature condition of artificial carbonatization nor the type of the source serpentinite. Gradual temperature increase from 50 $^{\circ}$C through 160 $^{\circ}$C to

200 $^{\circ}$C has influence on higher participation of carbonates (calcite, dolomite, magnesite) at the expense of acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite). Acid carbonates preferably grow at temperature 50 $^{\circ}$C while higher temperatures serve as a suitable environment for carbonates formation.
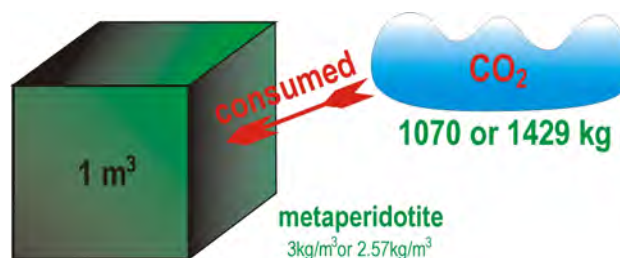
Fig. 7.11. Scheme of the volume of sequestered CO₂ in 1 m³ of metaperidotite.

7.8. Conclusion

The capability of metaperidotite (locality Hodkovce) to eliminate industrial CO_2 emissions has been verified by the experimental study of artificial carbonatization. Laboratory tests have been carried out on prepared samples of ultramafic rocks from above mentioned locality. The serpentinite was mixed with water at the temperature 22 $^{\circ}$C, when the pressure of carbon dioxide was changed from 0.1 to 0.3 MPa and the time from 5 to 20 hours during reactions. The acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite), as well as carbonates (calcite, dolomite, and magnesite) crystallized from filtrate with pH value of about 8, during 4-24 hours (in dependency on the varying temperatures).

This group of new minerals crystallized according to the following reactions:

$$serpentine + 3CO_2 + 6\,H_2O \xrightarrow{50^{\circ}C + 0.1\,MPa\,CO_2} 2\,nesquehonite + barringtonite + SiO_2 \qquad (6)$$

$$serpentine + diopside + olivine + 6CO_2 + 3H_2O \xrightarrow{160\,^{\circ}C\,or\,200\,^{\circ}C,\,+\,0.1MPa\,CO_2} hydromagnesite + magnesite + calcite + 5SiO_2 \qquad (7)$$
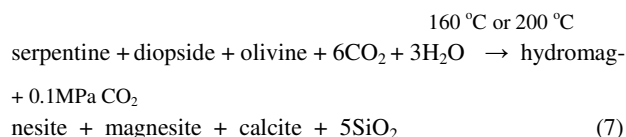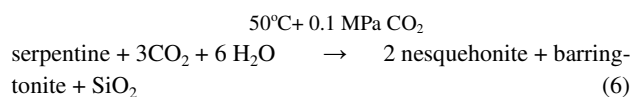
The reactions 6 and 7 served as the base for CO_2 weight calculation that resulted in the final conclusion - how many kg of carbon dioxide is capable 1 m^3 of serpentinite to bond in its volume, under different temperature regimes. In comparison of ideal mass of CO_2 liquidated in 1 m^3 of metaperidotite, the sequestered mass of the carbon dioxide from 1,070 kg to 1,429 kg does not depend neither on the temperature condition of artificial carbonatization nor on the type of the source rock. The gradual temperature increase from 50 $^{\circ}$C through 160 $^{\circ}$C to 200 $^{\circ}$C has influence on higher share of carbonates formation (calcite, dolomite, and magnesite) at the ex-

pense of acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite). Acid carbonates are dominating below temperature 50 $^{\circ}$C while higher temperatures serve as a suitable environment for carbonates formation.

Results of experimental study show that serpentinite rocks are a suitable eliminator of CO_2 especially in the eastern part of Slovakia. Achieved results represent a solid base for better understanding the artificial carbonatization.

8. Databases of Storage Capacities

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In this work we present selected geological structures that might be suitable for CO_2 storage. The geological structures (their boundaries) are available in the georeferenced form are presented in Table 8.1-8.5.

Although we are fully aware that we have not exhausted all the options which varied and complicated geological structure of the Slovak territory provides, we have selected a particular set of objects. In the case that development in the sphere of global warming causes the need to implement concrete actions in this issue, the Slovak Republic has prepared structures that could serve in the initial stage of the pilot project. For comparison, the average price of pilot projects currently being implemented in Europe vary between 80-120 M €. We have to note that these projects deal with the 'impact study' where the storage volume is not significant (<100 kt). Besides the classical "hydrodynamic approach" to CO_2 storage (extracted hydrocarbon deposits and regional aquifers), we developed the technology of mineral carbonatization. Advantage of this approach rests in the fact that some structures have a capacity allowing to move smoothly from the pilot (scale-up) stage to the industrial stage. Exceptions are objects of mineral carbonatization, which in terms of practical use "lag" behind depleted hydrocarbon deposits and regional aquifers in terms of their lesser scientific elaboration.

Within the database the objects were placed where it would be potentially possible (from the current point of view) to store carbon dioxide. The database is provided in the table form, where primary division refers to extracted hydrocarbon deposits and regional aquifers. Similarly, we lined up ultramafic rocks, with relevant properties. For the last group it should be noted that although our aim was to test all the essential bodies, in most cases only one technological sample represents one site. It is obvious that our assessment will certainly be vitiated due to the "random error", an unavoidable issue at this stage of research. Some sites with several samplings suggest that this factor has to be accounted for. The mineral sequestration is still only at the stage of laboratory research and thus we expect that in the near term, this gap will gradually fill up.

Tab. 8.1 Depleted hydrocarbon deposits

Num.	Name of storage site	Lithological - tectonic characteristic	Horizon	Depth of cap (m)	Collector thickness (m)	Number of boreholes
1.	Prukša (Ptr)					
		East Slovakian Basin, Lower Sarmatian, strongly faulted brachysyncline	3. Lower Sarmatian, fault block IX b.. Ptr. 21, 28, 29, 34	Ptr. 28-1,451, 29-1,503, 34-1,456.5	Ptr. 28-16.5, 29-5, 34-4	4
			4. Lower Sarmatian, fault block V.a, Ptr. 2, 5, 16, 22, 58	Ptr. 2-1,800, 16-1,794, 58-1,815	Ptr. 2-13, 16-17, 58-4	5
			4. Lower Sarmatian, fault block IXb, Ptr. 18, 21, 24, 28, 33, 34, 35, 36, 37, 43	Ptr. 21-1,476, 28-1,483, 33-1,499.5, 37-1,463	Ptr.21 - 5,5, 28 - 16, 33 - 8,5, 37 - 11	10
			4 a. Lower Sarmatiant, fault block IX b, Ptr. 24, 35, 37	Ptr. 24-1,521, 35-1,514, 37-1,508	Ptr. 24-24, 35-17, 37-28	3
			5. Lower Sarmatian, fault block VII b, Ptr. 7, 26, 55	Ptr. 7-1,784, 26-1,771, 55-1,771	Ptr. 7-18, 26-70, 55-4	3
			6. Lower Sarmatian, fault block IX b, Ptr. 4, 18, 21, 24, 28, 35, 36, 37, 43	Ptr. 18-1,730, 24-1,734, 35-1,737, 36-1,722, 37-1 733, 43-1,758	Ptr. 18-12, 24-11, 35-5, 36-5, 37-18, 43-4	9
2.	Stretava (Str)	East Slovakian Basin, Lower Sarmatian, brachyanticline, direction NNW/SSE, faulted by Močarany Topľa system faults	1. Lower Sarmatian, fault block VII, Str. 1, 3, 10, 11	Str. 1-1,146, 3-1,145	Str. 1-13, 3-9	4
			2. Lower Sarmatian, fault block VII, Str. 1, 3, 11	Str. 1-1,170, 3-1,169, 11-1,194	Str. 1-8, 3-6, 11-2	3
			3. Lower Sarmatian, fault block VII, Str. 1, 3, 11	Str. 1-1,210, 3-1,206,	Str. 1-4, 3-5	3
			3 b Lower Sarmatian, fault block VI-VII, Str. 1, 3, 11, 18, 48, 51	Str. 3-1302.5, 18-1,263, 48-1,246	Str. 3-10.5, 18-8.5, 48-6	6
			4. Lower Sarmatian, fault block IV, Str. 4, 13	Str. 4-1,282, 13-1,297	Str. 4-4.5, 13-5	2
			8. Lower Sarmatian, fault block II a, Str. 4, 12, 14, 15, 17, 35, 36, 38, 48	Str. 38-1,784.5, 48-1,850, 48-1,884	Str. 38-8.5, 48-22.5, 48-11	9

Num.	Name of storage site	Porosity (%)	Permeability (mD)	Temperature (°C)	Pressure (MPa)	Total dissolved solids	Overburden (type, thickness, deformation)	Capacity (kt)	Capacity type	Trap type
1.	Prukša (Ptr)	12.2	5.0-100	84.2	14.8	high	intact sandy, micaceous, stratified clay	389	effective	structural - stratigraphic
		14.9	n/a	102.8	19.5	high	sandy, micaceous stratified clay	289	effective	structural - stratigraphic
		15	10.0-30.0	86.6	15.2	high	sandy, micaceous stratified clay	572	effective	structural - stratigraphic
		12	5.0-50.0	88.2	13.4	high	sandy, micaceous stratified clay	321	effective	structural - stratigraphic
		15.6	n/a	101.8	18.9	high	sandy, micaceous stratified clay	97	effective	structural - stratigraphic
		10	10.0-100.0	99.8	18.4	high	sandy, micaceous stratified clay	332	effective	structural - stratigraphic
2.	Stretava (Str)	15	n/a	71.5	12.9	very high	clay, tuffite	201	effective	structural - stratigraphic
		18	n/a	71.5	12.8	very high	clay, tuffite	162	effective	structural - stratigraphic
		22	n/a	73.6	13.1	very high	clay, tuffite	373	effective	structural - stratigraphic
		22	n/a	77.5	13.7	very high	clay, tuffite	202	effective	structural - stratigraphic
		15	n/a	76.6	14	very high	clay, tuffite	187	effective	structural - stratigraphic
		18.4	n/a	107	26.9	very high	clay, tuffite	105	effective	structural - stratigraphic

Num.	Name of storage site	Lithological - tectonic characteristic	Horizon	Depth of cap (m)	Collector thickness (m)	Number of boreholes
			8. Lower Sarmatian, Block III b, Str. 40, 46	Str. 40-1,885, 46-1,935	Str. 40-10, 46-82	2
			5. Lower Sarmatian, VI, Str. 27, 29	Str. 27-1,589, 29-1,657	Str. 27-29, 29-6	2
3.	Bánovce nad Ondavou	East Slovakian Basin Badenian, Bánovce structure, faulted	9. Badenian, fault block XV, Bánovce 35	1,837	9	1
4.	Trhovište - Pozdišovce (Trh)	East Slovakian Basin, Badenian, brachyanticline structure, strongly faulted	16.Badenian, fault block VII, Trh 12, 16, 19, 32, 33, 41, Po-2, 10	Trh 12-1,214, 16-1,233	Trh 12-63.5, 16-21	8
			18. Badenian, block VII, Trh 12, 16, 21, 32, 33, 41, Po 2, 10	Trh 12-353, 16-1295, 41-1,332.5	Trh 12-2, 16-43, 41-8.5	8
			20. Badenian, fault block VII, Trh 12, 16, 21, 29, 32, 33, 41, Po 2, 10	Trh 12-1,411, 12-1,397.5, 41-1,419	Trh 12-33.5, 12-7, 41-29	9
			20.Badenian, fault block XI, Trh 31, 44, 46, 48	Trh 31-1,409, 31-1,388, 44-1,395, 46-1,402	Trh 31-89, 31-5, 44-7, 46-22	4
			22. Badenian, fault block VI.b, Trh 26	Trh 26-1,512.5	Trh 26-45	1
5.	Senné (Sen)	East Slovakian Basin, Sarmatian, elevation situated on the high fault zones of Močarany-Topľa fault belt	5.a Sarmatian, fault block I., Sen 18	Sen 18-1,594	Sen 18-6	1
			5.a Sarmatian, fault block II., Sen 3, 10	Sen 3-1,670, Sen 10-1,634	Sen 3-2, Sen 10-18	2
			6.Sarmatian, fault block III.a, Sen 4, 8, 21	Sen 4-1,769, Sen 8-1,775.5, Sen 21-1,725.5	Sen 4-6, Sen 8-18.5, Sen 21-3	3
			7. Sarmatian, fault block IIa, Sen 1, 5, 27, 36	Sen 1-1,739, Sen 5-1,759,5	Sen 1 - 26, Sen 5-22.5	4
			7. Sarmatian, block IV, Sen 7, 31, 35	Sen 35-1,854	Sen 35-6	3
			7. a Sarmatian, block IV, Sen 7, 31, 35	Sen 7-1,905, Sen 35-1,795	Sen 7-30, Sen 35-11	3
			8. Sarmatian block I.b., Sen 13, 25, 34	Sen 13-1,916, Sen 25-1,871	Sen 13-5.5, Sen 25-31	3

Num.	Name of storage site	Porosity (%)	Permeability (mD)	Temperature (°C)	Pressure (MPa)	Total dissolved solids	Overburden (type, thickness, deformation)	Capacity (kt)	Capacity type	Trap type
		18.4	n/a	110	29.5	very high	clay, tuffite	361	effective	structural - stratigraphic
		14	n/a	95	22.5	very high	clay, tuffite	84	effective	structural - stratigraphic
3.	Bánovce nad Ondavou	22	n/a	94.8	19.5	high	clay, tuffite	62	effective	structural
4.	Trhovište - Pozdišovce (Trh)	23	n/a	76.5	12.1	high	clayey deposit	474	effective	structural - stratigraphic
		19	n/a	80	13	high	clayey deposit	357	effective	structural - stratigraphic
		20	n/a	84	13.7	high	clayey deposit	142	effective	structural - stratigraphic
		18	n/a	83	13.9	high	clayey deposit	178	effective	structural - stratigraphic
		21.3	n/a	89	18.8	high	clayey deposit	296	effective	structural - stratigraphic
5.	Senné (Sen)	15.9	n/a	90	19.2	very high	clayey deposit	186	effective	structural - stratigraphic
		15.4	n/a	93.5	20	very high	intact, sandy micaceous stratified clay	185	effective	structural - stratigraphic
		14.81	n/a	100	21.6	very high	clay, claystone	135	effective	structural - stratigraphic
		13.8	n/a	99	23.8	very high	clay, claystone	354	effective	structural - stratigraphic
		22.3	n/a	103	24.9	very high	clay, claystone	4,982	effective	structural - stratigraphic
		17.3	n/a	103	23.7	very high	clay, claystone	391	effective	structural - stratigraphic
		26	n/a	102	27.8	very high	clay, claystone	143	effective	structural - stratigraphic

Num.	Name of storage site	Lithological - tectonic characteristic	Horizon	Depth of cap (m)	Collector thickness (m)	Number of boreholes
			8. Sarmatian, fault block II.b., Sen 6, 12, 16	Sen 6-1,990, Sen 12-1,986, Sen 16-1,959	Sen 6-8.5, Sen 12-9, Sen 16-5	3
			8. Sarmatian, fault block III.a, Sen 4, 8, 21, 38	Sen 8 – 1,986.5, Sen 21-1,976, Sen 38-1,916	Sen 8-41.5, Sen 21-3.5, Sen 38-135	4
			Badenian fault block I b, Sen 5, 12, 16	Sen 5-2,000, Sen 16-2,056	Sen 5-34, Sen 16-2	3
6.	Studienka (Stu)	Vienna Basin, Studienka elevation - a part of Láb-Lakšár. Nová Ves elevation belt	**1. Sarmatian, Stu 83, 84, 88, 98**	Stu 83-531, 84-536,5	Stu 83-6, 84-3,5	4
			Higher Bolívino - Bulimina horizon Late Badenian Stu 1, 6, 36, 39	965	157.5	4
			Bolívino - Bulimina horizon, Late Badenian, Stu 39	1,195	2.5	1
7.	Závod	Vienna Basin, Závod structure; brachyanticline, (Štefanov - Šaštín - Závod elevation belt)	**Middle Badenian, 1-6 Láb sand**	1,257	95	43
8.	Závod - South (Záv)	Vienna Basin, the north slope of Leváre gash	**1. Late Badenian, Záv 80**	1,372	4	1
9.	Závod Mesozoicum	Vienna Basin, Lower Golier nappe; brachyanticline	**Mesozoic II., central object, Záv. 73, 76, 85, 89, 90**	Záv 73-4,123, 76-4,175, 89 – 4,359	Záv 73-109, 76-65, 89-31	5
			Mesozoicum III., Záv 77	4,347	33	1
			Mesozoicum IV., Záv 79	4,365	155	1
			Mesozoicum V., Záv. 74, 78	Záv 74-4,390, 74-4,370, 78-4,053	Záv 73-30, 74-10, 78-19	2
10.	Gbely	Vienna Basin, elevation near Hodonín - Gbely fault	**Staré pole**	240	50	>100
			Nové pole	150	30	>100
11.	Jakubov (Jak)	Vienna Basin, depression zone	**Jakubov-starý, 8.Pannonian, Jak 5, 6, 7**	Jak 5-592, 6-605.5, 7-597	Jak 5-10, 6-1.5, 7-5	3
			Jakubov-starý, 2 Sarmatian, upper and lower object B, Jak 14, 39	Jak 14-716, 39-728	Jak 14-5.5, 39-2	2
			Jakubov-starý, Late Badenian, Jak 14	1,064	2	1

Num.	Name of storage site	Porosity (%)	Permeability (mD)	Temperature (°C)	Pressure (MPa)	Total dissolved solids	Overburden (type, thickness, deformation)	Capacity (kt)	Capacity type	Trap type
		0.19	n/a	107.5	28.5	very high	clay, claystone	129	effective	structural - stratigraphic
		13.3	n/a	109.1	26.6	very high	clay, claystone	230	effective	structural - stratigraphic
		n/a	n/a	116	30.3	very high	clay, claystone	130	effective	structural - stratigraphic
6.	Studienka (Stu)	25	n/a	28	5.04	high	clay	227	effective	structural
		25	n/a	53.5	9.8	high	sandy, marly clay	658	effective	structural
		20	28.24-102.82	50	10.7	high	sandy, marly clay	398	effective	structural
7.	Závod	25	0-1,379	55	13	high	marly clay	546	effective	structural
8.	Závod - South (Záv)	26	655.1	51.8	14.23	n/a	claystone, clay	612		structural
9.	Závod Mesozoicum	4	20.0-120	144.9	44.79	high	claystone	1 216	effective	structural
		2.3	28.24-102.82	143	43.68	high	claystone	153	effective	structural
		8.7	28.24-102.82	143	43.91	brine	claystone	70	effective	structural
		2.9	n/a	133	43.54	high	claystone	2,086	effective	structural
10.	Gbely	26	7,000-76,000	17	2.8	moderate	clay	9,378	effective	structural - stratigraphic
		31	n/a	15	1.5	moderate	clay	13	effective	structural - stratigraphic
11.	Jakubov (Jak)	33	800-1,500	27	6.2	high	sand	276	effective	structural - stratigraphic
		28.5	n/a	32	6.9	high	sandstone, sand	471	effective	structural - stratigraphic
		27	n/a	45	11.2	high	sandstone, sand	405	effective	structural - stratigraphic

Num.	Name of storage site	Lithological - tectonic characteristic	Horizon	Depth of cap (m)	Collector thickness (m)	Number of boreholes
11.	Jakubov - South	Vienna Basin depression zone, Láb elevation belt, brachyanticline	Jakubov North, Middle Badenian, Jak 41, 43, 45	Jak 41-1,596, 43-1,540.5, 45-1,566	Jak 41-5, 43-6, 45-17.5	3
			Late Badenian "b" sand, Jak 20, 21, 23, 27, 28, 30, 31	Jak 20-1,257, Jak 21-1,215.5, Jak 23-1,260, Jak 27-1,243.5, Jak 28-1,267, Jak 31-1,246	Jak 20-5.5, Jak 21-28, Jak 23-6, Jak 23-6, Jak 27-3.5, Jak 28-1.5, Jak 31-23.5	7
12.	Láb	Vienna Basin, Láb elevation	Láb horizon + Lower Badenian, East; Láb North - East + West	1,383	66	22
13.	Vysoká pri Morave (Vys)	Vienna Basin, brachyanticline elevation	2. Sarmatian, Vys 9, 21, 23, 24, 30, 31	680	20	6
			Late Badenian E, Vys 1, 2, 5, 8, 10, 14, 15, 18, 21, 22, 23, 25, 26, 27	1,300	80	14
14.	Jakubov - Dúbrava (Dub)	Vienna Basin, Láb elevation	2. Middle Badenian, Dub 6, 8, 10, 11, 13, 14, 15, 19, 23, 24, 25, 26, 27, 28, 29, 30, 45, 46	1,538	113	18
15.	Ivanka - Golianovo	Danube Basin, Komjatice Depression	Sarmatian	1,750	60	10
16.	Križovany nad Dudváhom - natural CO$_2$ deposit, planned underground gas storage site	Danube Basin, Blatné Depression, brachyanticline	Middle Badenian	960-1,060	45	?
17.	Horná Krupá	Danube Basin, Blatné Depression, brachyanticline, conglomerate	Eggenburgian	800	60	?
			Karpatian	600	110	?
18.	Trakovice	Danube Basin, Blatné Depression, brachyanticline, conglomerate, sandstone	Early Badenian, Middle Badenian	810	260	?
19.	Cífer	Danube Basin, Blatné Depression, brachyanticline, sandy conglomerate	Palaeogene, Karpatian, Middle Badenian,	1,500	200	?
20.	Báhoň	Danube Basin, Blatné Depression, brachyanticline, conglomerate	Middle Badenian	1,100	250	?
22.	Lipany	Inner Carpathian Palaeogene, intraformation breccia	Late Cretaceous, Jurassic	2,000	300	6

Num.	Name of storage site	Porosity (%)	Permeability (mD)	Temperature (°C)	Pressure (MPa)	Total dissolved solids	Overburden (type, thickness, deformation)	Capacity (kt)	Capacity type	Trap type
11.	Jakubov -South	26	365	62	15.1	very high	claystone	413	effective	structural - stratigraphic
		25	n/a	59	11.3	moderate	claystone	403	effective	
12.	Láb	19.3	n/a	71.5	14.5	high	claystone	2,476		structural
13.	Vysoká pri Morave (Vys)	30	107.9	36	6.9	high	claystone	389		structural - stratigraphic
		23.3	n/a	59.5	13.1	high	claystone	1,253		structural
14.	Jakubov - Dúbrava (Dub)	14.2	n/a	65	15.8	moderate	clay	131	effective	stratigraphic, pinch out
15.	Ivanka - Golianovo	12	20	?	?	?	clay	1 539	effective	structural
16.	Križovany nad Dudváhom - natural CO₂ deposit, planned underground gas storage site	27	?	57	11.7	very high	clay		effective	combined
17.	Horná Krupá	20	?	?	?	?	clay	5 294	effective	structural
		23	?	?	?	?	clay	9,706	effective	structural
18.	Trakovice	14	?	?	?	?	calcareous clay	9,056	effective	structural
19.	Cífer	20	?	?	?	?	clay	15,337	theoretical	structural
20.	Báhoň	14	?	?	?	?	claystone	18,547	theoretical	combined
22.	Lipany	3-5	100	100	?	?		10,000	theoretical	

Tab. 8.2 Local and regional aquifers

No.	Name of the locality	Polygon defining a cap of storage site (JTSK) X	Polygon defining a cap of storage site (JTSK) Y	Lithological-tectonic characteristic	Horizon	Depth of cap (m)	Collector thickness (m)	Number of boreholes	Porosity (%)	Permeability (mD)	Temperature (°C)
1	Zlatá Baňa	-249 245	-1 221 700	Slanské vrchy Mts.							
		-257 294	-1 221 201	Rhyolite and its pyroclastics in the Teriakovce Fm.	Early Karpatian	1,000-2,000	10-500	20	5		
		-256 006	-1 211 715								
		-245 522	-1 210 078	Rhyolite and its pyroclastics in the Teriakovce Fm.	Late Karpatian	700-1,200	10-300	20	5		
		-243 741	-1 216 579								
2	Zboj	-170 960	-1 209 263	Dukla Flysch		1,000 (?)	10-200	0	6		50
		-175 267	-1 206 583	Exo- and endocontact of interpreted andesite intrusion	Zboj Fm., Łupkow Fm., clay, sandstone						
		-170 549	-1 202 917	Volcanic gas saturating upper part of the intrusive body							
		-166 994	-1 204 648	Contact beetween Łupkow and Zboj Fms.							
3	Lipany	-282 642	-1 188 215	Šarišská vrchovina Highlands	Intraformational breccia	1,700-2,200	150-750	6	5		
		-281 246	-1 188 467	Base of Subtatric Group							
		-278 680	-1 189 313	Inner Carpathians Palaeogene							
		-277 436	-1 189 578								
		-274 764	-1 190 689								
		-275 214	-1 194 473								
		-277 119	-1 193 706								
		-277 727	-1 192 647								
		-283 813	-1 189 393								
4	Plavnica	-293 755	-1 179 802	Šarišská vrchovina Highlands	Intraformational breccia lower	1,700		2	5		
		-292 716	-1 179 011	Base of Subtatric Group	Intraformational breccia upper	2,306			5		
		-295 454	-1 177 994	Inner Carpathians Palaeogene							
		-297 771	-1 177 992								
5	Marcelová	-488 773	-1 330 272	Komárno marginal fault block	clayey limestone, calcareous shale, sandstone	1,035	162	1			50
		-483 459	-1 325 457	Carbonate - Early Triassic		1,405	354				
		-484 959	-1 324 179	Pelsö Unit							
		-490 160	-1 327 293								

No.	Name of the locality	Pressure (MPa)	Water chemistry	Overburden (type, thickness, deformation)	Bedrock (type, thickness, deformation)	Capacity (kt)	Capacity type	Trap type	Remark
1	Zlatá Baňa			siltstone, claystone / 200-500	siltstone, sandstone	17,300	theoretical	combined	Introduced porosity is the sober value, there are much more higher values. However data regarding permeabilities are missing.
				siltstone, claystone / 500	siltstone, claystone	7,800	theoretical	combined	
2	Zboj			claystone mostly; ca 1,000	fractured	13,500-27,000	theoretical	combined	The collector is supposed in the exo and endocontacts; in own intrusive body (upper part) and within the fractured boundary between Łupkow and Zboj Fm.; The capacity has been calculated for sweep coefficient 0.02 and 0.04.
3	Lipany			1,700 clay	100 Keuper mostly	4,000-10,000	theoretical	lithological	Horizon contains a little deposit of gas and crude oil, where could be stored about 500 kT of CO_2.
4	Plavnica			claystone, 1,700	claystone	3,100	theoretical	lithological	
				claystone 2,300	claystone; Fatricum unit en block	2,100	theoretical	lithological	
5	Marcelová	12	Na-Cl, 90g . l^{-1}			70,000	effective	structural	Closed structure. The calculated capacity is derived from the calculation of water reserves for both horizons together

Tab. 8.3 Mineral carbonatization A

Locality	Type of rock	Sample labelling	Content of mineral components in weight % containing appropriate chemical components for CO₂ sequestration	Potential for CO₂ reaction expressed by content of Mg and Ca oxides in weight %	Quantity of rock with entirely amorphoused minerals per tonne for its fixation to the:	
					magnesite	hydromagnesite
Hodkovce	serpentine	HO-1	serpentine mineral 77.8 olivine + pyroxene 12.6	$MgO = 36.06$ $CaO = 0$	2.54	3.174
	serpentine	HO-2	serpentine mineral 80.3 olivine + pyroxene 9.9	$MgO = 36.73$ $CaO = 0$	2.493	3.116
Rudník	serpentine	RU-1	serpentine mineral 67.6 olivine + pyroxene 19.0	$MgO = 34.75$ $CaO = 0$	2.635	3.294
	serpentine	RU-2	serpentine mineral 76.6 olivine + pyroxene 12.5	$MgO = 36.47$ $CaO = 0$	2.511	3.138
Jasov	serpentine	JA-1	serpentine mineral 78.5 olivine + pyroxene 9.7	$MgO = 36.23$ $CaO = 0$	2.527	3.159
Dobšiná	serpentine	S-1	serpentine mineral 88.7 olivine + pyroxene 0	$MgO = 36.09$ $CaO = 0$	2.538	3.171
Komárovce	serpentine	KO-1/2	serpentine mineral 65.7 olivine + pyroxene 25.2	$MgO = 39.72$ $CaO = 0$	2.305	2.881
	serpentine	KO-1/11	serpentine mineral 87.0 olivine + pyroxene 3.6	$MgO = 38.64$ $CaO = 0$	2.37	2.962
	serpentine	KO-1/16	serpentine mineral 70.4 olivine + pyroxene 19.8	$MgO = 39.73$ $CaO = 0$	2.305	2.881
Breznička	serpentine	BR-1	serpentine mineral 85.9 olivine + pyroxene 3.5	$MgO = 36.90$ $CaO = 0$	2.482	3.102
Miglinc	serpentine	MI-1	serpentine mineral 86.6 olivine + pyroxene 3.2	$MgO = 35.80$ $CaO = 0$	2.558	3.197

Tab. 8.4 Mineral carbonatization B

Locality	Type of rock	Geological material represented by the sample labelled	Equation of reactivity of mechanically and thermally activated rocks with CO_2 $(y = k \cdot Ln(x) + q)$	Character of the new carbonate product after 6 hours of carbonation	Mineral composition of the newly created product after 6 hours of carbonation	
					hydromagnesite	amorphous phase
Hodkovce	serpentine	HO-1	$y = 4.0184.Ln(x) + 18.4420$	hydromagnesite		7,8
	serpentine	HO-2	$y = 5.8460.Ln(x) + 16.8350$	hydromagnesite	90	10
Rudník	serpentine	RU – 1	$y = 5.1263.Ln(x) + 21.9540$	hydromagnesite	82	18
	serpentine	RU - 2	$y = 0.5388.Ln(x) + 21.4010$	hydromagnesite	91.6	8.4
Jasov	serpentine	JA - 1	$y = 1.9931.Ln(x) + 13.2130$	hydromagnesite	66.7	33.3
Dobšiná	serpentine	S - 1	$y = 2.9346.Ln(x) + 26.8460$	hydromagnesite	90.3	9.7
	serpentine	KO – 1/2	$y = 0.8591.Ln(x) + 19.9790$	hydromagnesite	90.3	9.7
Komárovce	serpentine	KO – 1/11	-	-	-	-
	serpentine	KO – 1/16	$y = 1.9059.Ln(x) + 16.1040$	hydromagnesite	78.1	21.9
Breznička	serpentine	BR – 1	$y = 1.8597.Ln(x) + 10.2020$	hydromagnesite	72.5	17.5
Miglinc	serpentine	MI – 1	$y = 0.9813.Ln(x) + 16.6950$	hydromagnesite	89.2	10.8

Explanation:
CaO - the entire contents of input samples is bound to $CaCO_3$, it means zero content is "free" for the reaction of CaO with CO_2
y - increment in mass yield of the newly established carbonate product in weight % in relation to the material inlet of the sample;
k - coefficient
x - duration of action of carbon dioxide in hours;
q - increment in mass yield of the newly established carbonate product in weight % After one hour carbonatization;
LN - natural logarithm

Tab. 8.5 Mineral carbonatization C

Locality	Type of rock	Sample	Chemical composition of the newly created product after 6 hours of carbonatization (%)					Regime of carbonatization			Quantity (t) of mechanically and thermally activated rocks per 1 tonne of CO_2	
								p (CO_2 pressure)	T (temperature of the environment)			
			Fe_2O_3	CaO	MgO	CO_2	Loss by ignition %			t (exposure time CO_2)	MgO from serpentine	Increment < 1 %
Hodkovce	serpentine	HO-1	0.04	0.98	43.02	34.7	54.1			6 MPa, 22 °C, 6 hours	4.086	8.511/24 hours
	serpentine	HO-2	0.06	0.26	43.09	33.9	54.6			6 MPa, 22 °C, 3 hours	3.88	7.030/36 hours
Rudník	serpentine	RU11	0.39	1.63	41.4	30.9	48.5			6 MPa, 22 °C, 6 hours	5.069	6.743/30 hours
	serpentine	RU - 2	0.1	0.97	42.3	34.5	52.7			6 MPa, 22 °C, 6 hours	4.173	11.874/6 hours
Jasov	serpentine	JA-1	0.5	2.03	39.9	25.1	43.6			6 MPa, 22 °C, 6 hours	4.346	14.616/12 hours
Dobšiná	serpentine	S-1	0.04	1.02	42.8	34	54.8			6 MPa, 22 °C, 6 hours	3.599	7.518/18 hours
	serpentine	KO-1/2	0.24	0.97	41.8	34	52.8			6 MPa, 22 °C, 6 hours	4.52	12.343/6 hours
Komárovce	serpentine	KO-1/11	-	-	-	-	-			-	-	-
	serpentine	KO-1/16	1.19	2.27	40.6	29.4	46.7			6 MPa, 22 °C, 6 hours	4.343	12.745/12 hours
Breznička	serpentine	BR-1	0.22	3.52	39.3	27.3	45			6 MPa, 22 °C, 6 hours	3.959	17.921/12 hours
Miglinc	serpentine	MI-1	0.09	0.7	42.8	33.6	53.6			6 MPa, 22 °C, 6 hours	3.717	14.397/6 hours

Explanations: The values in the **second column from the right** prove for MgO from serpentine mineral reaction (chemical analysis) into hydromagnesite, because according X-ray analysis the unreacted olivine + pyroxene remained in the filter cake. The values in the **first column from the right** prove for the fact that the increment in mass yield of the newly formed product calculated according to given formula, after given time period is less than 1%, whereas the new product contains hydromagnesite.

9. Legislative aspects of the CO$_2$ storage

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A broad range of problems accompanying the final part of the CCS chain - geological disposal - must have a sufficient support in the functional legislation setting up the factual, temporal and environmental aspects of long-term and safe storage of CO$_2$. The current situation can be characterized as follows:

9.1 European framework

A Working Group of the European Commission (EC) for the Capture and Geological Storage has been originated in the framework of the Second European Climate Change Programme (ECCP II). The Group stressed the need to establish policy and regulatory frameworks for CCS. The Communication on Sustainable Power Generation from Fossil Fuels of January 2007 set out an action plan for the Commission, which requires a design of an appropriate regulatory framework. Following the European Council meeting in Brussels in March in 2007, have been established the main objectives:

– to reduce greenhouse gas emissions by 2020 at least on 20 %; in the case of an international agreement the emissions reduction should reach 30 %;

– to achieve 20 % share of renewables in the EU energy consumption by 2020, including 10 % share of biofuels.

Furthermore, the Member States and the Commission, in the context of meeting the above mentioned objectives, press for a necessary technical, economic and regulatory framework to bring environmentally safe capture and geological storage of carbon in industrial use.

To achieve these objectives, including guaranteeing energy security and combat climate change, the European Commission presented on the 23rd January 2008 an integrated climate and energy package, which consisted of four legislative proposals:

1. Directive on the Promotion of Energy from Renewable Sources,

2. Revision of the Emissions Trading Directive,

3. Decision setting targets for individual Member States to reduce emissions in sectors that are not a subject to emissions trading,

4. Directive on Carbon Capture and Storage.

The planned Directive on Carbon Capture and Storage was designed to promote this new technology, whereas, the EU cannot omit fossil fuels (coal) as a major source of energy in the near future. An intention was to create a legislative framework that will encourage an investment in the CCS and set up parameters so that emission emitters of energy generation took a better position to promote this technology, instead of buying emission permits.

Subsequently a Working Group (to the European Commission) started with the assessment of the draft of the Directive, which proclaimed intention to support the development of demonstration projects - repositories on which to test out the technology provided, or with EU assistance this technology would be gradually introduced into industrial applications.

The first meeting of the Working Group to the European Commission took place on January 28, 2008, in Brussels.

The Ministry of the Environment was entrusted to represent the Slovak Republic by compilation of the Directive. Directly in the creation process were involved B. Antal, Section of Geology and Natural Resources from above mentioned Ministry and Ľ. Kucharič, as an expert on the CCS issue from the State Geological Institute of Dionýz Štúr, Bratislava.

Fig. 9.1. Deputies of the Slovak Republic during break in the Working Group meeting in the Justus Lipsius building in Brussels (from the right: B. Antal, Ľ. Kucharič)

In total, 19 workshops took place and one bilateral meeting with representatives of the Bureau. Finishing works on the Directive were conducted at the Commission level. A total of 10 completed draft versions of

the Directive had been processed, till the Directive passed in the European Parliament. Finally the DIRECTIVE 2009/31/EC was approved by the European Parliament on the 23rd of April 2009.

The deadline for member states to bring into force the laws, regulations and administrative provisions of the CCS Directive was June 25, 2011.

Documentation about expansion of the CCS legislation into EU countries is given in the following text (Shogenova, et al., 2013):

By the end 2011 the transposition of the Directive into national law was approved by the European Commission (EC) in Spain only, but was approved at national/jurisdictional level in 12 more countries (Austria, Denmark, Estonia, France, Greece, Ireland, Italy, Latvia, Lithuania, Slovakia, Sweden, The Netherlands). Romania, Bulgaria, Portugal, Slovenia, three regions of Belgium and United Kingdom finished transposition of the CCS Directive at the national level in spring 2012. Implementation in the UK was completed in February 2012 and by end March 2012, implementation at national level was also completed in Bulgaria, Portugal and Romania. The European Commission had assessed national submissions of CCS legal acts transposing the Directive, and approved these in Denmark, the Netherlands, Italy, France, Lithuania, Malta, Portugal, Romania and Slovakia by June 2012. Czech Republic, Hungary and Finland finalised publishing their laws in May-July 2012. The CCS Directive has been transposed into German law at the end of August 2012. One region of Belgium, Croatia, Norway and Poland had not finished the transposition of the CCS Directive by December 2012.

Italy, France and The Netherlands permit CO_2 storage (except for seismic areas in Italy) and support demonstration projects via their climate/energy strategy. Lithuania, Slovakia and part of Belgium permit CO_2 storage, but they do not explicitly support the development of CO_2 storage projects. Eight countries prohibited CO_2 storage in their territory, except for research, either permanently (Estonia, Ireland and Finland) or temporarily (Austria, Czech Republic, Latvia, Poland and Sweden). Onshore CO_2 storage is forbidden until 2020 in Denmark. Storage of limited amount of CO_2 only can be permitted up to 2030 in Bulgaria and up to 2018 in Germany. Italy, Greece and Belgium do not permit storage in proscribed areas.

Norway and Poland, countries with sufficient storage capacity that support demonstration projects, had not finished the CCS Directive transposition process by December 2012. Altogether 20 operating, developing and planned CCS pilot and demonstration projects, including capture and full chain CCS, have been identified in nine European countries. Results of the CCS Directive transposition in Denmark and the unfavourable climate of opinion in Germany resulted in the abandonment of two planned onshore projects by Vattenfall in these countries. The process of transposing the CCS Directive into national law and its assessment by the EC will be continued and reported to the European Parliament in 2013.

9.2 Slovak framework

A new law regarding geological storage of CO_2 had to be formed within two years after the approval by the EP. Creation of the law has been implemented under the auspices of the Ministry of the Environment with cooperation with the Ministry of Economy including the Main Mining Office and stakeholders from the industrial sphere. The works were carried out according the time schedule, set by the European Commission. A delay against the deadline was two weeks only, due to rather complicated process of clarifying positions of the relevant spheres.

Recent legislative regulation in force at the territory of Slovakia was transposed by applicable Act (258/2011 Coll.). Here is referred to that the Act does not apply to storage for the research purposes, development or testing of new equipment and technological processes with the total projected quantity of stored carbon dioxide less than 100,000 tons (§ 1 Object of the Act). However, these "small" research repositories are subject of environmental impact assessment (EIA) - to screening (24/2006 Collection of Laws, as amended by other regulations).

Another modification of the Act No. 245/2003 Coll. (on integrated prevention and control of environmental pollution, § 11. 1, letter l) introduces an obligation for the operation of the combustion plant with a rated electrical output of 300 MW and an assessment of conditions for storage of carbon dioxide in geological environment, in particular, whether:

1. Are there in the wider area of operation available appropriate sites under a special regulation?

2. Is an installation of carbon capture facility technically and economically feasible?

3. Are the equipments for the transport of carbon dioxide into the repository technically and economically feasible?

Under the current stagnant implementation process – a development of building repositories and also severely depressed trading permit to discharge CO_2, it can be expected that the European Commission extends the requirement to store CO_2 for the existing industrial equipment with lower rated electrical output in the near future.

The Act is based on the EC Directive and enacts a number of specific provisions. The first one is an actual site selection - practically only such structure can be used for permanent storage of CO_2, which can not be used for any other purposes.

The Act in a nutshell, defines the conditions for obtaining a storage permit, authorization applications to store, and change, check, update and revocation of authorisation of the storage permit. There are set up the criteria and procedures in the storage and monitoring of storage sites and associated surface and injection facilities and storage complex. The Act stipulates remedies and additional remedial measures when detecting leakage of carbon dioxide, or a significant deficiency in the storage complex is identified. Also a procedure for the closure of

storage and conditions after their abandonment of the transition of responsibility to the competent authority are set up. Moreover specific guidelines on how to choose the appropriate structure for storage and the monitoring procedure governing the storage site are introduced in the Annexes of this Act.

Very essential is a part devoted to the transition the responsibility for the storage site to the State and State rights to take control of the repository in certain cases and the impact of law on financial obligations created by the operator. Those provisions are directly related to the fact that the process of dissolution ("neutralization") of CO_2 in the collector takes several hundred years and the same is valid also for lasting obligations to monitor and ensure the repository and to perform the monitoring. This is connected with considerable financial claims, particularly on the state budget.

A more detailed description of certain specific features of the permanent storage of carbon dioxide in the geological environment (258/2011).

The actual wording of the Act is divided into 25 paragraphs and into the XI Articles that discuss laws that have affected the novel conceived Act; e.g.: Act. 44/1988 Coll. on the Protection and Use of Mineral Resources (the Mining Act); Act of the Slovak National Council No. 51/1988 Coll. (about Mining Activities, Explosives and State Mining Administration); Law No. 223/2001 Coll. (the Waste Act); Law No. 364/2004 Coll. On Water and amendment of the Slovak National Council. 372/1990 Coll. on Offences, as amended (Water Act); Act. 572/2004 Coll. on Emissions Trading; Law No. 24/2006 Coll. on Environmental Impact Assessment, etc. The Act itself contains two annexes, the first of which establishes the criteria and procedures for assessing the storage complex, while the second one is devoted to monitoring activities.

Under the Act No.569/2007 Coll., on Geological Works, carbon dioxide storage into geological environment has been incorporated into stage of the geological deposit survey (§ 3 letter h).

Storage site

As a storage site (§ 3) shall be considered an area of a geological unit into which carbon dioxide is stored and where associated superficial and injection facilities are built.

As a storage site cannot be considered a natural rock structure or an underground space that is reasonably preferred to the exploration, exploitation and storage of hydrocarbons, to geothermal utilisation, storage of radioactive wastes and other wastes in underground spaces, or for any other uses of underground storage for energy purposes, including options, that are strategic for the security of energy supply and renewable energy development.

Furthermore a rock structure with significant reserves of groundwater, including natural healing and natural

mineral resources and any collector of fresh water cannot be considered as a storage site. For storage complex is considered to be a repository and associated geological environment that must affect the overall integrity and security of storage.

The legislative financial demands on the process of storing

Claims for financial coverage of storage activities start at the beginning of approving permits for CO_2 storage, even in the stage of application for a storage permit. The applicant for a permit shall declare that he disposes of sufficient financial resources to build storage, to carry out operation and disposal to address any significant deficiencies. An adequate bank account with access rights has to be established by governing body for this purpose. This adequate financial security determines a District Mining Authority due to size of the repository and the planned volume of CO_2 to be saved. These funds are from the time of issue of the storage permit available to the relevant District Mining Office, which, if the conditions specified in the permit, may dispose of them for predetermined purposes (§ 16).

An amount of "reasonable financial provision" may decrease in the event of smooth course of the operation when the process of gradual creation of "Financial Compensation" (§ 17) can be open. Provided during repository operation the primary containment of storage site will change and thereby the risk of CO_2 leakage will be increased, the volume of financial security will be increased adequately.

Upon completion of repository operation, after its sealing, and removing unnecessary equipment, and before moving responsibility for the storage site to the relevant District Mining Authority, this stipulates appropriate level of funding to ensure the tightness of the primary storage site and storage complex monitoring for a period of 30 years (§ 17). Funds in excess of the specified amount shall be released in favour of the former operator. A financial compensation (§ 17) generates an operator during repository operation annually charged to expenditure at the height indicated by the relevant District Mining Office to ensure the tightness of the primary storage site and storage complex monitoring.

The obligation transition

The relevant District Mining Authority on its own initiative or at the request of the operator assumes responsibility for the site and performs the duties related to the monitoring and remedial and other measures to ensure its tightness (§ 15) under the following conditions:

• The tightness of the primary structure was ensured and at least twenty years have passed after repository closure, if the District Mining Office doesn't provide otherwise. Furthermore, the financial liability has been fulfilled (§ 17) and the storage site has been sealed and the injection facilities have been removed.

• In the case where an operator is unable or does not want to eliminate leakage or significant deficiency or fails to respect terms of a storage or his actions will increase the risk of leakage or it does not address it, the District Mining Authority shall withdraw an authorization the operator to store and take over the responsibilities associated with the management and operation of the repository (§ 8). All costs associated with the removal of significant deficiencies to seal the repository go to the expense of the operator or to the detriment of established financial compensation and financial security (§ 16, § 17).

In conclusion of the legislative excursion a practical overview of the legislative process repository is introduced here:

1) At the very beginning the first step of a repository building is search and exploration of suitable geological structure, which is possible only on the basis of an exploration permit - exploration of that site is considered as deposit geological survey, and only person authorized to carry out survey can perform it (569/2007 Geological Act)

2) Upon completion of the geological exploration of the geological structure or in the event of conversion to a varying degree of exploitation shall be made a settlement of reserves (§ 34a, 44/1988 Coll. Mining Act) with the calculation of the volume of the structure and the **subsequent approval and the decision of the Commission for approval of mineral reserves** of the Ministry of Environment.

3) Subsequently, the holder of exploration area or mining area to the present geological structure applies for the "**Certificate of Appropriateness of Natural Rock Structure** and underground space for the storage of gases and liquids" at the Ministry of Economy (Government Regulation No. 107/2010).

4) A future operator shall submit the storage permit to the relevant District Mining Authority – if the storage site is located in the area belonging two District Mining Authorities, the one decides on the territory of whom the greater part of the complex is located (258/2011 Coll. 44/1988 Coll.)

9.3 Summary

Specific provisions of the Directive (Article 4, Site Selection), which have not been translated into a transposed law, is the right of a Member State to determine the areas from which storage sites may be selected for the permanent storage of CO_2 as well as to allow or disallow the storage in parts of its territory or in the whole extension of its territory.

The provision is partly reflected in the Geological Act (§ 24, 569/2007 Coll.), which enacts the obligation of the State (Ministry of Environment) to define areas in which it is allowed a) to conduct geological exploration on hydrocarbons (oil and combustible gas), b) to establish in natural rock structures and underground spaces permanent storage of carbon dioxide in geological environment. Specified areas are published by the Ministry of Environment on its website with an annual update (www.minzp.sk).

There is no mention in the Directive adopted by the EP and EC regarding permitting or prohibiting a Member State for CO_2 transport through its territory or export CO_2 emissions in a case when CO_2 storage is forbidden on its territory. The problem will be surely a subject of conflicts of interest at the time of development of the method of deposition and building CCS infrastructure.

Solving these issues as well as others that will be emerge during a stage of demonstration projects will be a subject of the Directive revision, which is established for the March 31, 2015 (Article 38, review), in the frame of which the Commission has an obligation based on experiences of the implementation of the CCS and the related technological advancement and the latest scientific knowledge to assess a topicality of the Directive adopted by the European Parliament on the 23rd April 2009 and, where necessary, to submit a proposal for its revision**.**

10. Present situation and real prospects of CCS in Slovakia and in the World

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In the present situation, despite the Slovak Act on CO_2 storage in force we do not expect specific activities in this issue in the near future. Some options might take shape in the case of getting funding for a pilot project. For this purpose, we have selected a number of structures - Láb, Marcelová, Stretava and Ptrukša, as well as Vysoká - Zwerndorf, where, however, the problem of joint ownership with the neighbouring states - Austria, has to be faced.

In terms of timeline the carbon dioxide storage is a long-term process as documented by the following picture.

- from a practical point of view, in relation to depleted hydrocarbon deposits there exist a possibility of some potential for CO_2 storage in Slovak conditions because still remains open an issue of additional exploitation of depleted gas deposits by Enhanced Gas Recovery methodology (EGS). This technology could be interesting in the future in Slovakia, particularly in relation to the aforementioned gas deposit Vysoká - Zwerndorf, where it remains unexploited "interesting volume" of methane.

- This issue is interesting in terms of the use of CO_2 as a cushion gas in the underground reservoirs of natural gas, because thank to its greater density it takes up less space than methane (CH_4/CO_2 ratio is 1:0.6), which provides undisputed benefits at an enlargement of the active volume capacity of planned reservoirs. However, the problem of the separation of two gases in the reservoir still remains open.
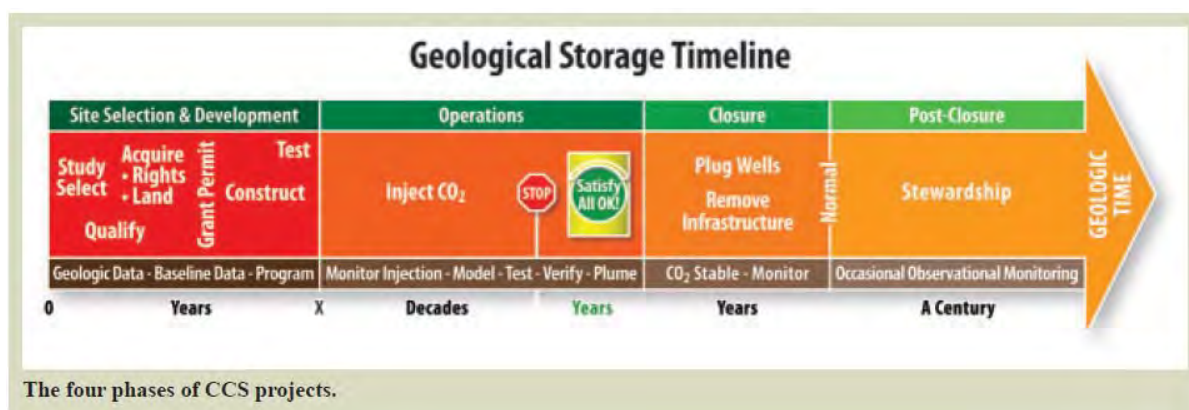

Fig. 10.1 Geological storage timeline (Source www.CO_2Capture project.org)

- Another problem is a very low price of the permits to emit (EUA), which are sensitive to the global economic situation. Even in the mid of 2011 these price levels amounted over 16 €/t, but under the influence of the economic crisis by May 2013 they got below the level of 3 €/t, which virtually eliminates at least approximate expert estimates for the costs associated with CO_2 storage. In this context, the financing or part-financing of a pilot project for the private sector, even if a theoretical profit considered, the sale of the extracted gas is very illusory. (According to theoretical calculations a price of 1 tonne of CO_2 storage should amount to 25-30 € - only operating costs). In this way, the CCS for business is actually non-attractive.

- The storage potential of 37.840 Mt was estimated in the area of the Danube Basin. Due to the fact that it is only a small aquifer deposits space, it can be expected that the quite optimistic storage potential will be reduced within further progress of work. However, this area is not negligible when considering the shift of CCS methodology into practice.

- At the pessimistic estimate the regional aquifers are set on 180,300 kt, in the optimistic estimate on 236, 200 kt of stored CO_2. These numbers relative to the annual quota for Slovakia (NAPL - National Allocation Plan) of 40 Mt are not at all overwhelming.

- We pointed out prospective assessment of the hydrocarbons potential of the NE part of Slovakia (Rudinec,

Tab. 10.1 CCS projects in the world - presence and near future (according to Global CCS Institute)

Asset Lifecycle Stage	Project Name	Description	State / District	Country	Volume CO_2
Operate	Century Plant	Occidental Petroleum, in partnership with Sandridge Energy, is operating a gas processing plant in West Texas that at present can capture 5 Mtpa of carbon dioxide for use in enhanced oil recovery. Capture capacity will be increased to 8.5 Mtpa in 2012.	Texas	UNITED STATES	8.4 Mtpa*
Operate	Enid Fertilizer CO_2-EOR Project	Since 1982, the Enid Fertilizer plant has sent around 680,000 tonnes per annum of carbon dioxide to be used in enhanced oil recovery operations in Oklahoma.	Oklahoma	UNITED STATES	0.68 Mtpa
Operate	Great Plains Synfuel Plant and Weyburn-Midale Project	About 3 Mtpa of carbon dioxide is captured from the Great Plains Synfuel plant in North Dakota. Since 2000 the carbon dioxide has been transported by pipeline into Canada for enhanced oil recovery in the Weyburn Field, and since 2005 in Midale Field.	Saskatchewan	CANADA	3 Mtpa
Operate	In Salah CO_2 Storage	In Salah is a fully operational CCS project in Algeria. Since 2004, around 1 million tonnes per annum of carbon dioxide are separated from produced gas, transported by pipeline and injected for storage in a deep saline formation.	Wilaya de Ouargla	ALGERIA	1 Mtpa
Operate	Shute Creek Gas Processing Facility	Around 7 million tonnes per annum of carbon dioxide are recovered from ExxonMobil's Shute Creek gas processing plant in Wyoming, and transported by pipeline to various oil fields for enhanced oil recovery. This project has been operational since 1986.	Wyoming	UNITED STATES	7 Mtpa
Operate	Sleipner CO_2 Injection	Sleipner is the second largest gas development in the North Sea. Carbon dioxide is separated from produced gas at Sleipner T and reinjected into a deep saline formation above the hydrocarbon reservoir zone. This project has been in operation since 1996.	North Sea	NORWAY	1 Mtpa
Operate	Snøhvit CO_2 Injection	The Snøhvit offshore gas field and related CCS activities have been in operation since 2007. Carbon dioxide separated from the gas produced at an onshore liquid natural gas plant is reinjected into a deep saline formation below the reservoir zones.	Barents Sea	NORWAY	0.7 Mtpa
Operate	Val Verde Natural Gas Plants	This operating enhanced oil recovery project uses carbon dioxide sourced from the Mitchell, Gray Ranch, Puckett, Pikes Peak and Terrell gas processing plants and transported via the Val Verde and CRC pipelines.	Texas	UNITED STATES	1.3 Mtpa
Execute	Air Products Steam Methane Reformer EOR Project	This project in construction will capture more than 1 million tonnes per year of carbon dioxide from two steam methane reformers to be transported via Denbury's Midwest pipeline to the Hastings and Oyster Bayou oil fields for enhanced oil recovery.	Texas	UNITED STATES	1 Mtpa
Execute	Alberta Carbon Trunk Line ("ACTL") with Agrium CO_2 Stream	Agrium's fertiliser plant in Alberta is currently being retrofitted with a carbon dioxide capture unit. Around 585,000 tonnes per annum of carbon dioxide will be captured and transported via the Alberta Carbon Trunk Line (ACTL) for enhanced oil recovery.	Alberta	CANADA	Up to 0.59 Mtpa (initially 0.29 Mtpa)
Execute	Alberta Carbon Trunk Line ("ACTL") with North West Sturgeon Refinery CO_2 Stream	Up to 1.2 million tonnes per annum of carbon dioxide will be captured at this new heavy oil upgrader in Alberta. In partnership with Enhance Energy, the carbon dioxide will be transported via the Alberta Carbon Trunk Line (ACTL) for enhanced oil recovery.	Alberta	CANADA	1.2 Mtpa
Execute	Boundary Dam Integrated Carbon Capture and Sequestration Demonstration Project	SaskPower is currently retrofitting a coal-based power generator with carbon capture technology near Estevan, Saskatchewan. When fully operational in 2014, this project will capture around 1 million tonnes per annum of carbon dioxide.	Saskatchewan	CANADA	1 Mtpa
Execute	Gorgon Carbon Dioxide Injection Project	This component of a larger gas production and LNG processing project will inject 3.4 to 4.1 million tonnes of carbon dioxide per annum into a deep geologic formation. Construction is under way after a final investment decision was made in September 2009.	Western Australia	AUSTRALIA	3.4 - 4.1Mpa
Execute	Illinois Industrial Carbon Capture and Storage Project	The project will capture around 1 million tonnes per annum of carbon dioxide from ethanol production. Carbon dioxide will be stored approximately 2.1 km underground in the Mount Simon Sandstone, a deep saline formation.	Illinois	UNITED STATES	1 Mtpa
Execute	Kemper County IGCC Project	Mississippi Power (Southern Company) is constructing an air-blown 582 Mwe IGCC plant using a coal-based transport gasifier. Up to 3.5 million tonnes per annum of carbon dioxide will be captured at the plant and used for enhanced oil recovery.	Mississippi	UNITED STATES	3.5 Mtpa
Execute	Lost Cabin Gas Plant	This project will retrofit the Lost Cabin natural gas processing plant in Wyoming with CCS facilities, capturing around 1 million tonnes per annum of carbon dioxide to be used for enhanced oil recovery.	Wyoming	UNITED STATES	1 Mtpa
Execute	Quest	Quest will capture up to 1.2 million tonnes of carbon dioxide per annum from the Scotford upgrader, and transport it by pipeline for injection into a deep saline formation.	Alberta	CANADA	1.08 Mtpa
Define	Belchatów CCS	PGE EBSA intends to integrate a carbon capture plant into a new built 858 MW unit at the Belchatow Power Plant, capturing around 1.8 million tonnes per annum of carbon dioxide.	Łódź	POLAND	1.6 - 1.8 Mtpa
Define	Coffeyville Gasification Plant	CVR Energy is developing a new compression facility at its fertiliser plant in Kansas. The plant currently produces approximately 850,000 tonnes of carbon dioxide which will be transported to the mid-continental region for use in enhanced oil recovery.	Kansas	UNITED STATES	0.85 Mtpa
Define	Don Valley Power Project	Early in 2011, 2Co Energy acquired the Don Valley Power Project, a 650 MW IGCC facility in South Yorkshire. The project intends to capture around 4.8 million tonnes of carbon dioxide per annum for enhanced oil recovery or geological storage.	South Yorkshire	UNIT. KINGDOM	4.75 Mtpa
Define	ESI CCS Project	This project proposes to capture around 800,000 tonnes per annum of carbon dioxide from a steel plant in the Industrial City of Abu Dhabi by 2015. The project is being developed as part of the Abu Dhabi CCS Network (Masdar).	Abu Dhabi	UNITED ARAB EMIRATES	0.8 Mtpa
Define	Green Hydrogen	Air Liquide has built a new hydrogen plant in Rotterdam. The installation of a cryogenic purification unit at the plant, capturing up to 550,000 tonnes per annum of carbon dioxide, is under evaluation.	Zuid-Holland	NETHERLANDS	0.5 Mtpa
Define	Hydrogen Energy California Project (HECA)	SCS Energy has taken over the HECA project from Hydrogen Energy. The new design will be a 400 Mwe polygeneration plant capturing 3 million tonnes per annum of carbon dioxide for enhanced oil recovery and production of urea.	California	UNITED STATES	3 Mtpa

Asset Lifecycle Stage	Project Name	Operation Date	Facility Details	Capture Type	Transport Length	Transport Type	Storage Type	Project URL
Operate	Century Plant	2010	Natural Gas Processing	Pre-Combustion (Gas Processing)	256 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.oxy.com/
Operate	Enid Fertilizer CO_2-EOR Project	1982	Fertiliser Production	Pre-Combustion	225 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.kochfertilizer.com/
Operate	Great Plains Synfuel Plant and Weyburn-Midale Project	2000	Synthetic Natural Gas	Pre-Combustion	315 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.cenovus.com/
Operate	In Salah CO_2 Storage	2004	Natural Gas Processing	Pre-Combustion (Gas Processing)	14 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.insalahco2.com/
Operate	Shute Creek Gas Processing Facility	1986	Natural Gas Processing	Pre-Combustion (Gas Processing)	190 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.exxonmobil.com
Operate	Sleipner CO_2 Injection	1996	Natural Gas Processing	Pre-Combustion (Gas Processing)	0 km	Direct injection	Offshore Deep Saline Formations	http://www.statoil.com/en/
Operate	Snøhvit CO_2 Injection	2008	Natural Gas Processing	Pre-Combustion (Gas Processing)	152 km	Onshore to offshore pipeline	Offshore Deep Saline Formations	http://www.statoil.com/en/
Operate	Val Verde Natural Gas Plants	1972	Natural Gas Processing	Pre-Combustion (Gas Processing)	132 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.exxonmobil.com/
Execute	Air Products Steam Methane Reformer EOR Project	2013	Hydrogen Production	Post-Combustion	101-150 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.airproducts.com/
Execute	Alberta Carbon Trunk Line ("ACTL") with Agrium CO_2 Stream	2014	Fertiliser Production	Pre-Combustion	240 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.agrium.com/
Execute	Alberta Carbon Trunk Line ("ACTL") with North West Sturgeon Refinery CO_2 Stream	2015	Oil Refining	Pre-Combustion	240 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.northwestupgrading.com/
Execute	Boundary Dam Integrated Carbon Capture and Sequestration Demonstration Project	2014	Power Generation	Post-Combustion	100 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.saskpower.com/
Execute	Gorgon Carbon Dioxide Injection Project	2015	Natural Gas Processing	Pre-Combustion (Gas Processing)	7 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.chevronaustralia.com/
Execute	Illinois Industrial Carbon Capture and Storage Project	2013	Chemical Production	Industrial Separation	1.6 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.adm.com/
Execute	Kemper County IGCC Project	2014	Power Generation	Pre-Combustion	75 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.mississippipower.com/
Execute	Lost Cabin Gas Plant	2013	Natural Gas Processing	Pre-Combustion (Gas Processing)	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.conocophillips.com/
Execute	Quest	2015	Hydrogen Production	Pre-Combustion	84 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.shell.ca/
Define	Belchatów CCS	2017	Power Generation	Post-Combustion	101-150 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.bot.pl/
Define	Coffeyville Gasification Plant	2013	Fertiliser Production	Pre-Combustion	112 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.cvrenergy.com/
Define	Don Valley Power Project	2016	Power Generation	Pre-Combustion	425 km for EOR, 175km to alternative saline site	Onshore to offshore pipeline	Enhanced Oil Recovery	http://www.2coenergy.com/
Define	ESI CCS Project	2015	Iron and Steel Production	Industrial Separation	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.esi-steel.com/
Define	Green Hydrogen	2016	Hydrogen Production	Industrial Separation	26 km	Onshore to offshore pipeline	Offshore Depleted Oil and Gas Reservoirs	http://www.airliquide.com/
Define	Hydrogen Energy California Project (HECA)	2017	Power Generation	Pre-Combustion	6.4 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.hydrogenenergycalifornia.com/

Asset Lifecycle Stage	Project Name	Description	State / District	Country	Volume CO₂
Define	Hydrogen Power Abu Dhabi (HPAD)	This project will convert natural gas into hydrogen and carbon dioxide. The 380 MW hydrogen power plant will generate over 5 per cent of all Abu Dhabi's current power generation capacity. Captured carbon dioxide will be used for enhanced oil recovery.	Abu Dhabi	UNITED ARAB EMIRATES	1.7 Mtpa
Define	Lake Charles Gasification	Leucadia and Lake Charles Cogeneration plan to build a gasification plant to produce synthetic natural gas from petcoke. Around 4.5 million tonnes per annum of carbon dioxide will be captured at the plant and used for enhanced oil recovery.	Louisiana	UNITED STATES	4.5 Mtpa
Define	Medicine Bow Coal-to-Liquids Facility	Medicine Bow Fuel and Power propose to build a greenfield, coal-to-liquids facility that will produce up to 21,000 barrels of gasoline per day, and capture up to 3.6 million tonnes of carbon dioxide per annum for enhanced oil recovery.	Wyoming	UNITED STATES	3.6 Mtpa
Define	NRG Energy Parish CCS Project	NRG Energy proposes to capture more than 1.4 million tonnes per annum of carbon dioxide from its Parish coal-fired power plant in Fort Bend County, Texas, for use in enhanced oil recovery.	Texas	UNITED STATES	1.4 - 1.6 Mtpa
Define	OXYCFB 300 Compostilla Project	When operating at full scale, the Compostilla project would capture around 1.1 million tonnes per annum of carbon dioxide from a 300 Mwe oxyfuel power plant. The project's 30 MWth pilot started operating in December 2011.	Leon	SPAIN	1.1 Mtpa
Define	Porto Tolle	This project will capture around 1 million tonnes per annum of carbon dioxide from a new build coal-based power station using post-combustion capture. The carbon dioxide will be injected into a deep saline formation in the northern Adriatic Sea.	Veneto	ITALY	1 Mtpa
Define	Rotterdam Opslag en Afvang Demonstratieproject (ROAD)	E.ON and GdF Suez propose to capture around 1.1 million tonnes per annum of carbon dioxide from the flue gases of a new coal-based power plant that is currently being constructed within the industrial port of Rotterdam.	Zuid-Holland	NETHERLANDS	1 Mtpa
Define	Spectra Fort Nelson CCS Project	Carbon dioxide sourced at the Fort Nelson natural gas-processing plant will be injected into a nearby saline formation at a depth of approximately 2,200 metres. Injection rates will ramp up to 1.2 to 2 million tonnes per annum of carbon dioxide.	British Columbia	CANADA	2.2 Mtpa
Define	Swan Hills Synfuels A" In-Situ Coal Gasification/Power Generation Project"	This project intends to build a 300 MW combined cycle power plant, using syngas produced at an adjacent coal gasification unit. Around 1.4 million tonnes per annum of carbon dioxide will be captured for enhanced oil recovery.	Alberta	CANADA	1.2 - 1.4 Mtpa
Define	Taylorville Energy Center	The Taylorville Energy Center is a proposed 602 MW IGCC power plant located in Illinois. Around 3 million tonnes per annum of carbon dioxide will be captured at the plant and stored in onshore deep saline formations or used in enhanced oil recovery.	Illinois	UNITED STATES	1.92 Mtpa
Define	Tenaska Trailblazer Energy Center	Tenaska is developing a site near Sweetwater, Texas, to construct a supercritical pulverised coal-based power plant designed to capture up to 85-90 per cent of the carbon dioxide that would otherwise enter the atmosphere.	Texas	UNITED STATES	5.75 Mtpa
Define	Texas Clean Energy Project	Summit Power Group is developing a 400 MWe IGCC polygeneration plant capturing 2.5 million tonnes of carbon dioxide to be used for enhanced oil recovery in the Permian Basin in West Texas.	Texas	UNITED STATES	2.5 Mtpa
Define	ULCOS - Blast Furnace	The project at a steel mill proposes to capture carbon dioxide from a coal and metallurgical coke facility for iron and steel production. The carbon dioxide would be transported by pipeline and stored in a deep saline formation.	Lorraine	FRANCE	0.7 Mtpa
Evaluate	Bow City Power Project	The Bow City Power Project is a proposed super critical 1,000 Mwe coal-based power plant in Alberta, incorporating post-combustion carbon capture and storage. Around 1 million tonnes per annum of carbon dioxide will be captured for enhanced oil recovery.	Alberta	CANADA	1 Mtpa
Evaluate	C.GEN North Killingholme Power Project	C.GEN is proposing a new IGCC plant in north Lincolnshire that would capture around 2.5 million tonnes per annum of carbon dioxide feeding into the National Grid transport and storage network. The project is part of the Yorkshire Forward initiative.	North Lincolnshire	UNITED KINGDOM	2.5 Mtpa
Evaluate	CarbonNet Project	The Victorian Government is developing this CCS hub project in the Australian state of Victoria. Carbon dioxide collected from various capture facilities would be stored in an offshore deep saline formation.	Victoria	AUSTRALIA	1 Mtpa
Evaluate	Cash Creek Generation	The ERORA Group proposes to build a hybrid IGCC project in Owensboro, Kentucky. It will produce about 565 MW as well as synthetic natural gas. The plant will capture about 2 million tonnes per annum of carbon dioxide for enhanced oil recovery.	Kentucky	UNITED STATES	2 Mtpa
Evaluate	Emirates Aluminium CCS Project	This project proposes to capture around 2 million tonnes per annum of carbon dioxide from two natural gas-based power plants by 2017. The project is being developed as part of the Abu Dhabi CCS Network (Masdar).	Abu Dhabi	UNITED ARAB EMIRATES	2 Mtpa
Evaluate	Full-scale CO₂ Capture Mongstad (CCM)	StatoilHydro and the Norwegian government entered into an implementation agreement to develop carbon dioxide capture solutions at the Mongstad natural gas power plant, with a view to capture and store up to 1 million tonnes per annum of carbon dioxide.	Hordaland	NORWAY	1 Mtpa
Evaluate	FutureGen 2.0 Oxy-Combustion Large Scale Test	FutureGen 2.0 is an initiative to demonstrate state-of-the-art combined cycle turbine by repowering an existing 200 Mwe unit at Ameren's coal-based power plant in Meredosia, Illinois, with advanced oxy-combustion technology.	Illinois	UNITED STATES	1.3 Mtpa
Evaluate	Getica CCS Demonstration Project	Getica will capture around 1.5 million tonnes per annum of carbon dioxide from a lignite based power plant. The carbon dioxide captured at the plant will be stored in onshore deep saline formations.	Gorj County	ROMANIA	1.5 Mtpa
Evaluate	HuaNeng GreenGen IGCC Project	GreenGen Co. proposes to build a coal-based energy system that includes hydrogen production, electricity generation and carbon capture. The carbon dioxide captured at the site will be used for enhanced oil recovery.	Tianjin	CHINA	2 Mtpa
Evaluate	Indiana Gasification	This coal gasification plant project would include a methanation process to produce pipeline quality synthetic natural gas (SNG). The carbon dioxide captured at the plant would be used for enhanced oil recovery.	Indiana	UNITED STATES	4.5 Mtpa
Evaluate	Kentucky NewGas	This project is a new build mine to mouth coal to synthetic natural gas plant in Kentucky proposing to capture around 5 million tonnes per annum of carbon dioxide for enhanced oil recovery or for storage in a deep saline formation.	Kentucky	UNITED STATES	5 Mtpa

Asset Lifecycle Stage	Project Name	Operation Date	Facility Details	Capture Type	Transport Length	Transport Type	Storage Type	Project URL
Define	Hydrogen Power Abu Dhabi (HPAD)	2018	Power Generation	Pre-Combustion	201-250 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.hydrogenenergy.com/
Define	Lake Charles Gasification	2014	Synthetic Natural Gas	Pre-Combustion	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.leucadia.com/
Define	Medicine Bow Coal-to-Liquids Facility	2015	Coal-to-liquids (CTL)	Pre-Combustion	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.dkrwadvancedfuels.com/
Define	NRG Energy Parish CCS Project	2015	Power Generation	Post-Combustion	130 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.nrgenergy.com/
Define	OXYCFB 300 Compostilla Project	2015	Power Generation	Oxyfuel Combustion	120 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.compostillaproject.es/
Define	Porto Tolle	2015	Power Generation	Post-Combustion	101-150 km	Onshore to offshore pipeline	Offshore Deep Saline Formations	http://www.zeportotolle.com/
Define	Rotterdam Opslag en Afvang Demonstratieproject (ROAD)	2015	Power Generation	Post-Combustion	26 km	Onshore to offshore pipeline	Offshore Depleted Oil and Gas Reservoirs	http://www.road2020.nl/en
Define	Spectra Fort Nelson CCS Project	2016	Natural Gas Processing	Pre-Combustion (Gas Processing)	35 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.spectraenergy.com/
Define	Swan Hills Synfuels A" In-Situ Coal Gasification/Power Generation Project"	2015	Synthetic Natural Gas	Pre-Combustion	51 – 100 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.swanhills-synfuels.com/
Define	Taylorville Energy Center	2017	Power Generation	Pre-Combustion	8 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.cleancoalillinois.com/
Define	Tenaska Trailblazer Energy Center	Not specified	Power Generation	Post-Combustion	201-250 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.tenaskatrailblazer.com/
Define	Texas Clean Energy Project	2015	Power Generation	Pre-Combustion	≤50 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://texascleanenergyproject.com/
Define	ULCOS - Blast Furnace	2016	Iron and Steel Production	Industrial Separation	51-100 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.ulcos.org/en/
Evaluate	Bow City Power Project	2018	Power Generation	Post-Combustion	≤50 km	Onshore to onshore pipeline	Enhanced Oil Recovery	www.bowcitypower.ca
Evaluate	C.GEN North Killingholme Power Project	2015	Power Generation	Pre-Combustion	151-200 km	Onshore to offshore pipeline	Offshore Deep Saline Formations	http://www.cgenpower.com/
Evaluate	CarbonNet Project	2018	Power Generation	Not Decided	51-100 km	Onshore to offshore pipeline	Offshore Deep Saline Formations	http://www.invest.vic.gov.au/
Evaluate	Cash Creek Generation	2015	Power Generation	Pre-Combustion	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.erora.com/
Evaluate	Emirates Aluminium CCS Project	2018	Power Generation	Post-Combustion	351-400 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.tapco.ae/
Evaluate	Full-scale CO$_2$ Capture Mongstad (CCM)	2020	Power Generation	Post-Combustion	Not decided	Onshore to offshore pipeline	Offshore Deep Saline Formations	http://www.statoil.com/en/
Evaluate	FutureGen 2.0 Oxy-Combustion Large Scale Test	2016	Power Generation	Oxyfuel Combustion	≤50 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.futuregenalliance.org/
Evaluate	Getica CCS Demonstration Project	2015	Power Generation	Post-Combustion	40 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.ispe.ro/en/
Evaluate	HuaNeng GreenGen IGCC Project	2020	Synthetic Natural Gas	Pre-Combustion	151-200 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.chng.com.cn/eng/
Evaluate	Indiana Gasification	2015	Synthetic Natural Gas	Pre-Combustion	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.leucadia.com/
Evaluate	Kentucky NewGas	2018	Synthetic Natural Gas	Pre-Combustion	Not specified	Onshore to onshore pipeline	Various Storage Options Being Considered	www.kentuckynewgas.com

Asset Lifecycle Stage	Project Name	Description	State / District	Country	Volume CO$_2$
Evaluate	Korea-CCS 1	This project proposes to capture around 1 million tonnes of carbon dioxide per annum from an integrated circulating fluidized bed combustion (CFBC) power plant for storage in deep saline formations.	Not Decided	KOREA	1 Mtpa
Evaluate	Mississippi Gasification (Leucadia)	Leucadia Energy and Mississippi Gasification propose to capture around 4 million tonnes per annum of carbon dioxide from a petcoke gasification plant in Moss Point, Mississippi. The carbon dioxide will be used for enhanced oil recovery.	Mississippi	UNITED STATES	4 Mtpa
Evaluate	Peterhead Gas CCS Project	Around 1 million tonnes per annum of carbon dioxide will be captured by Peterhead Power Station, one of Scotland's largest plants. The carbon dioxide is likely to be transported offshore and stored in depleting gas fields in the North Sea.	Aberdeenshire	UNIT. KINGDOM	0.97 Mtpa
Evaluate	Quintana South Heart Project	A 175 MW IGCC electric power generating facility in southwest North Dakota. The facility will convert lignite into hydrogen and power, capturing up to 2.1 million tonnes per annum of carbon dioxide for enhanced oil recovery.	North Dakota	UNITED STATES	2.1 Mtpa
Evaluate	Riley Ridge Gas Plant	Denbury Resources proposes to retrofit a natural gas processing plant under construction in Wyoming to capture around 2.5 million tonnes per annum of carbon dioxide for enhanced oil recovery.	Wyoming	UNITED STATES	2.5 Mtpa
Evaluate	Sinopec Shengli Oil Field EOR Project	Around 1 million tonnes per annum of carbon dioxide will be captured from an existing power plant in Shangdong and used for enhanced oil recovery.	Shandong	CHINA	1 Mtpa
Evaluate	South West CO$_2$ Geosequestration Hub (formerly Collie-South West Hub)	This project proposes to develop a transport and storage hub collecting carbon dioxide captured from various facilities in Western Australia. The project aims to store more than 2 million tonnes per annum of carbon dioxide in deep saline formations.	W. Australia	AUSTRALIA	2-3 Mtpa
Evaluate	Southland Coal to Fertiliser Project	Solid Energy and Ravensdown are jointly developing a coal to fertiliser plant capturing around 1.2 million tonnes per annum of carbon dioxide for storage in a deep saline formation. The plant is projected to begin operations in 2018.	Southland	NEW ZEALAND	1 Mtpa
Evaluate	Surat Basin CCS Project (formerly Wandoan)	Around 1 million tonnes per annum of carbon dioxide would be captured from this 250 MWe power plant in Central Queensland, and stored in deep non-potable aquifers.	Queensland	AUSTRALIA	1 Mtpa
Evaluate	Teesside Low Carbon (formerly Eston Grange CCS Plant)	Progressive Energy proposes to develop a new IGCC power plant with pre-combustion carbon capture at 400MWe on a snfield site in Teesside. This project is part of the North East CCS Cluster initiative.	North East England	UNIT. KINGDOM	2.5 Mtpa
Evaluate	White Rose CCS Project (formerly UK Oxy CCS Demonstration)	Alstom UK, Drax Power and National Grid are jointly developing a new 426 MW oxy-fired plant in North Yorkshire which would capture around 2 million tonnes per annum of carbon dioxide. The project is part of the Humber CCS Cluster.	N. Yorkshire	UNIT. KINGDOM	2 Mtpa
Identify	Shenhua / Dow Chemicals Coal to Chemicals Plant Project (Yulin)	This project developed by Dow Chemical proposes to build a coal to chemicals production plant capturing 2-3 million tonnes of carbon dioxide per annum for use in enhanced oil recovery.	Shaanxi	CHINA	2-3 Mtpa
Identify	Captain Clean Energy Project (formerly Caledonia Clean Energy Project)	Summit Energy proposes to replicate its Texas Clean Energy Project concept at this new build plant in Scotland. Carbon dioxide captured at the plant would be stored or used for enhanced oil recovery in the North Sea.	Scotland	UNIT. KINGDOM	Not specified
Identify	Daqing Carbon Dioxide Capture and Storage Project	This project proposes to capture more than 1 million tonnes per annum of carbon dioxide from a new coal-fired power plant near Daqing City.	Heilongjiang	CHINA	1 Mtpa
Identify	Dongguan Taiyangzhou IGCC with CCS Project	Dongguan Taiyangzhou Power Corporation intends to construct an 800 MW IGCC plant capturing up to 1 million tonnes of carbon dioxide per annum to be stored in depleted oil and gas reservoirs.	Guangdong	CHINA	1 Mtpa
Identify	Dongying Carbon Dioxide Capture and Storage Project	The China Datang Group is developing a new power generation project with CCS, with a planned capture capacity of around 1 million tonnes per annum of carbon dioxide, which will then be used for enhanced oil recovery.	Shandong	CHINA	1 Mtpa
Identify	Industrikraft Møre AS Norway	The proposed Sargas Stargate 250 Gasfired Powerplant in Norway would capture more than 1.4 million tonnes per annum of carbon dioxide. The project could be operational in 2016.	Møre og Romsdal	NORWAY	1.4-1.6 Mtpa
Identify	Jilin Oil Field EOR Project (Phase 2)	More than 800,000 tonnes per annum of carbon dioxide from a natural gas processing plant are planned to be injected into the Jilin oil field for enhanced oil recovery by 2015.	Jilin	CHINA	0.8-1 Mtpa
Identify	Korea-CCS 2	This project proposes to capture 1 million tonnes of carbon dioxide per annum from an oxyfuel or IGCC power plant. The carbon dioxide captured at the plant would be shipped for injection into a deep saline formation.	Not Decided	KOREA	1 Mtpa
Identify	Lianyungang IGCC with CCS Project	This project will consist of a 1200 MW IGCC power plant and 2 x 1300 MW supercritical power plant capturing up to 1 million tonnes of carbon dioxide per annum. Synthetic natural gas and chemicals will be co-produced at this plant.	Jiangsu	CHINA	1 Mtpa
Identify	Maritsa Thermal Power Plant CCS Project	This project proposes to capture 2.5 million tonnes per annum of carbon dioxide from an existing lignite-based thermal power plant in Bulgaria. The plant belongs to the Maritsa Iztok Complex, which is the largest energy complex in South Eastern Europe.	Stara Zagora	BULGARIA	2.5 Mtpa
Identify	Sargas Green Power Plant Malta	Sargas AS proposes to build a new power plant in Malta that would capture around 1.2 million tonnes per annum of carbon dioxide. The project could be operational in 2017.	Delimara	MALTA	1.2 Mtpa
Identify	Shanxi International Energy Group CCUS project	This project will involve the construction of a new, super-critical coal-fired power plant with oxyfuel combustion capturing more than 2 to 3 million tonnes per annum of carbon dioxide.	Shanxi	CHINA	2-3 Mtpa
Identify	Shen Hua Ningxia Coal to Liquid Plant Project	Shenhua Group proposes to build a new coal-to-liquids plant that would capture around 2 million tonnes per annum of carbon dioxide. Possible storage options are currently under evaluation.	Ningxia	CHINA	2 Mtpa
Identify	Shenhua Ordos CTL Project	This project intends to capture around 1 million tonnes of carbon dioxide per annum from an existing coal-to-liquids facility by 2020. It is the second phase of the operating pilot-scale Ordos Shenhua DCL plant CCS Project.	Inner Mongolia	CHINA	1 Mtpa

Asset Lifecycle Stage	Project Name	Operation Date	Facility Details	Capture Type	Transport Length	Transport Type	Storage Type	Project URL
Evaluate	Korea-CCS 1	2017	Power Generation	Post-Combustion	251-300 km	Ship/Tanker	Offshore Deep Saline Formations	http://www.kepco.co.kr/eng/
Evaluate	Mississippi Gasification (Leucadia)	2015	Synthetic Natural Gas	Pre-Combustion	176 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.denbury.com/
Evaluate	Peterhead Gas CCS Project	2017	Power Generation	Post-Combustion	102 km	Onshore to offshore pipeline	Offshore Depleted Oil and Gas Reservoirs	http://www.sse.com/
Evaluate	Quintana South Heart Project	2017	Power Generation	Pre-Combustion	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.greatnorthernpower.com/
Evaluate	Riley Ridge Gas Plant	2015	Natural Gas Processing	Pre-Combustion (Gas Processing)	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.denbury.com/
Evaluate	Sinopec Shengli Oil Field EOR Project	2017	Power Generation	Post-Combustion	51-100 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://english.sinopec.com/
Evaluate	South West CO$_2$ Geosequestration Hub (formerly Collie-South West Hub)	2017	Fertiliser Production	Pre-Combustion	51-100 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.dmp.wa.gov.au/
Evaluate	Southland Coal to Fertiliser Project	2018	Fertiliser Production	Pre-Combustion	51-100 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.coalnz.com/
Evaluate	Surat Basin CCS Project (formerly Wandoan)	2020	Power Generation	Post-Combustion	151-200 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.wandoanpower.com.au
Evaluate	Teesside Low Carbon (formerly Eston Grange CCS Plant)	2016	Power Generation	Pre-Combustion	225 km	Onshore to offshore pipeline	Offshore Deep Saline Formations	http://www.estongrange.co.uk/
Evaluate	White Rose CCS Project (formerly UK Oxy CCS Demonstration)	2016	Power Generation	Oxyfuel Combustion	Not specified	Onshore to offshore pipeline	Offshore Deep Saline Formations	http://www.whiteroseccs.co.uk/
Identify	Shenhua / Dow Chemicals Coal to Chemicals Plant Project (Yulin)	Not specified	Chemical Production	Industrial Separation	≤50 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.dow.com/
Identify	Captain Clean Energy Project (formerly Caledonia Clean Energy Project)	2018	Power Generation	Pre-Combustion	Not specified	Onshore to offshore pipeline	Enhanced Oil Recovery	http://www.summitpower.com/
Identify	Daqing Carbon Dioxide Capture and Storage Project	Not specified	Power Generation	Oxyfuel Combustion	Not specified	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.china-cdt.com/en/index.html
Identify	Dongguan Taiyangzhou IGCC with CCS Project	Not specified	Power Generation	Pre-Combustion	101-150 km	Onshore to onshore pipeline	Onshore Depleted Oil and Gas Reservoirs	http://www.dgpowerfuel.com/english/
Identify	Dongying Carbon Dioxide Capture and Storage Project	Not specified	Power Generation	Not Decided	≤50 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.china-cdt.com/en/index.html
Identify	Industrikraft Möre AS Norway	2016	Power Generation	Post-Combustion	Not specified	Combination (pipeline and shipping)	Not specified	http://sargasnearzero.com/
Identify	Jilin Oil Field EOR Project (Phase 2)	2015	Natural Gas Processing	Pre-Combustion (Gas Processing)	151-200 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://www.petrochina.com.cn/Ptr/
Identify	Korea-CCS 2	2019	Power Generation	Not Decided	251-300 km	Ship/Tanker	Offshore Deep Saline Formations	http://www.kepco.co.kr/eng/
Identify	Lianyungang IGCC with CCS Project	Not specified	Power Generation	Pre-Combustion	201-250 km	Onshore to onshore pipeline	Enhanced Oil Recovery	http://english.cas.cn/
Identify	Maritsa Thermal Power Plant CCS Project	2020	Power Generation	Post-Combustion	Not specified	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.bgenh.com/en/
Identify	Sargas Green Power Plant Malta	2017	Power Generation	Post-Combustion	351-400 km	Ship/Tanker	Enhanced Oil Recovery	http://sargasnearzero.com/
Identify	Shanxi International Energy Group CCUS project	Not specified	Power Generation	Oxyfuel Combustion	Not specified	Not Specified	Various Storage Options Being Considered	http://en.sxgjny.com/Singlelist.aspx?tp=cominfo&catalogID=8
Identify	Shen Hua Ningxia Coal to Liquid Plant Project	Not specified	Coal-to-liquids (CTL)	Industrial Separation	201-250 km	Onshore to onshore pipeline	Various Storage Options Being Considered	http://www.csclc.com.cn/ens/index.shtml
Identify	Shenhua Ordos CTL Project	2020	Coal-to-liquids (CTL)	Industrial Separation	201-250 km	Onshore to onshore pipeline	Onshore Deep Saline Formations	http://www.shenhuagroup.com.cn/english/

* per annum

- 1989) as confirmed by Zboj borehole results. We have contributed to these results not only by CCS input, but also further added value has been achieved in the potential importance of this site with Au-Ag base metal ore mineralization, as well as the extension of its potential into geothermal research, as one of the renewable energy sector. The study of appropriate structures is an undeniable benefit to further identification or forecasting of other raw materials, suitable for the needs of the economy.

- Similarly, open remains the issue of the marketable J - Br waters of an enclosed structure Marcelová, while carbon dioxide could serve as a mean for their pushing out on the surface.

- The most important outcome of the benefits of technological and geological research is finding and proof of gaseous carbon dioxide storage using geological materials from different localities of Slovakia in laboratory conditions, whereas the CO_2 is permanently and stably bound in new products, in which the newly formed carbonates (mainly hydromagnesite, calcite and aragonite) thermodynamically stabilize carbon dioxide prior to permanent storage.

- According to the results obtained by carbonatization the most promising material for mineral sequestration of CO_2 is serpentine rock containing about 37% of MgO component, bound mainly to serpentine minerals - chrysotile, lizardite and antigorite, or the olivine minerals - forsterite and fayalite, or it can be a rock containing wollastonite.

- The lowest costs according purpose-made feasibility study of the CO_2 capture and storage using the mineral sequestration were achieved using olivine as an input geological material - 54 US$/t CO_2, 64 US$/t CO_2 using wollastonite and 78 US$/t CO_2 using serpentine (O'Connor, 2005, and Gerdemann, 2007).

- According to our findings to capture one tonne of carbon dioxide an average of 2.6 tonnes of amorphous serpentine rock is needed; the average cost of this quantity will be 616 €/2.6 tonnes of rock.

- One tonne of carbon dioxide binds to 1.92 tonnes of $MgCO_3$ (formation of fine-grained newly precipitated magnesium carbonate), which value as a potential white inorganic filler in the case of $CaCO_3$ compensation may be at least around 390 €/t (price of untreated precipitated calcium carbonate).

- The next key fact is that due to the carbonatization of investigated materials (in high-pressure reactor) the hazardous waste turns to other waste in terms of waste classification.

The aim of the analysis was to contribute to the debate on the high costs incurred in the mineral sequestration. These are undisputable, but it is possible to reduce them by the price of the final carbonatization product, which might find its use in the industry. At present, it is difficult to quantify the ecological aspects of this way of storage.

It should be noted that often used cliché about the costs of the hydrodynamic storage regime, moving in the range of 30-40 €/t of CO_2, represents only the net operating costs, without giving the costs of the investment, which is a bit misleading. The investment costs for the transport facilities are extremely high - approximately 1.1 million € /km of pipeline (Hendriks et al., 2004) and represent a significant increase in the cost item and we still do not include the cost of sequestration technology.

Ultimately, the use of the results of CO_2 sequestration by carbonatization research in a laboratory-scale in a high-pressure reactor can contribute in the near future to reduce the amount of CO_2 emitted into the atmosphere and also to reduce and change the properties of the stored quantities of waste material, thereby significantly contributing to the protection of the environment as a whole. The technology can be a good complement to hydrodynamic technology and a way how to get secondary sources of minerals (quartz, magnesite, iron, nickel ...).

To illustrate the overall situation in the world, we present a summary Table of the sources of Global Institute (Australia), which summarizes all the CCS activities already underway, or planned in the next future. In spite of limitations generated by the economic crisis it is clear that the issue is hot. The Table describes in a comprehensive manner the operated or planned repositories. In addition to the geographical location it presents a process and method of CO_2 capture. It is obvious that meanwhile 8 storage objects at industrial scale are being operated. Annual volume fluctuates around 1 Mt store. Clearly dominating factor is the connection of storage with EOR (Enhanced Oil Recovery) - additional exploitation of already depleted oil deposits, because the economic benefits of the obtained residual reserves reduce significantly the financial costs of the CCS technology. Lengths of pipelines from the source are certainly interesting as well as a distance of emissions source to the repository. We leave a more detailed analysis of the Table on the reader, who can get additional info by visiting the respective website.

11. Conclusions and Recommendations

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Despite the fact that since 25 July 2011 the Slovak Act on underground storage of CO_2 has been in force, (No.258/2011 of the Code), certainly a considerable amount of time is needed until this important legislative instrument will be applied in the practical sphere.

The monograph has assessed depleted hydrocarbon deposits, local and regional aquifers, and mafic and ultramafic rocks that may be suitable for CO_2 storage.

All the objects that could be considered are included in the database, which provides the essential parameters that are available, including an estimate of storage capacity.

In terms of performance criteria the most appropriate are depleted hydrocarbon deposits. However, within the West-Carpathians territory they do not represent significant objects in terms of sufficient capacity. Those structures with calculated capacity which we could assign to "effective" ones allow some objects to be used for the purposes of the pilot project (Stretava, Ptrukša, Láb, Marcelová), but storage of industrial importance (annual volume of injected gas 500 kt - 1 (Mt) with a lifetime of 15-20 years cannot be considered except the Marcelová site.

The Marcelová structure should provide effective capacity for storing 70 Mt of CO_2 while extracting highly-mineralized brine containing economically interesting amounts of iodine and bromine. The highly-mineralized water exploitation (90 g.l^{-1}) could reduce to a certain extent the costs for CO_2 storage. Even if the estimated amount is too optimistic (based on the calculation of reserves of mineral waters), it is still interesting for capacity reasons and what is important from the point of security, the location in a seismically active area does not affect tightness of the reservoir. The CO_2 behaviour in the reservoir was predicted using hydrogeochemical modelling.

The sufficient storage capacity appears to have the deposit Vysoká - Zwerndorf in the Vienna Basin, shared by Slovakia and Austria. At the Slovak territory the deposit is depleted and flooded. According to our calculations 11.7 Mt of CO_2 can be stored at the Slovak side within so-called 'g' sand (base of Middle Badenian), which already produces reflections at industrial scale (pilot project could be implemented in the overlying horizons). At this point we would like to emphasize that at the Austrian side we can assume by the size of the deposit virtually doubled storage space. Non-negligible are residual methane reserves in the deposit, which could be exploited after mastering the EGR technology; but still this will definitely take several years of research.

Larger capacity estimates we assume within the Danube Basin, but here we are dealing with local storage in aquifers of identified small gas deposits. Although the estimated capacities are of the order of about 10 Mt, despite our very "sober" assessment, we must remember that these are "theoretical" capacities that require further work, which results in terms of capacity pyramids usually lead to diminished capacities. From the point of view of capacity the deposit Báhoň could be considered; of course, further work is needed to define the volume of the aquifer in detail.

In the case of the deposits of natural gases Križovany nad Dudváhom (CO_2) and Cífer (N_2) which are included among underground methane reservoirs, the question is where the original gases will be deposited (or used?), if they will be replaced by methane (e.g., the Križovany structure contains about 6 Mt of CO_2).

Since CCS is very costly, it is useful if the costs incurred could be at least partially covered by added value.

Similarly considered could be the Lipany site, where geothermal water from the Fatricum unit is planned to be exploited for recreational purposes. However, it contains a high amount of natural CO_2 to be disposed of. We suggest to store the carbon dioxide potentially in the overlying aquifer, situated near the base of the Inner Carpathian Palaeogene, with the possible additional exploitation of small deposits of methane and its use for the purpose of recreational facilities. The site has the features of potential industrial storage, but this requires further technical verification work.

Similarly interesting capacity has the Zlatá Baňa area in the Slanské vrchy Mts. The intention to store CO_2 within porous products of rhyolitic volcanism is not common, the implementation, however, requires a number of additional data.

At the Zboj site in the north-easternmost tip of Slovakia, we deduced a number of conclusions based on the interpretation of newly identified magnetic anomalies. In addition to the findings, leading to fundamental issues of geological setting, it is possible to deduce conclusions leading to the application sphere and not only to the prob-

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lems of CO_2 storage, but also to metallogenetic sphere. In any case the result may "provoke" potential candidates for business plans in hydrocarbon and metallogenetic issues.

The aforementioned structures are in our opinion the most significant findings in the framework of the research and we stress them because they have (except the Zboj site) very close affinity to the real situation.

Another interesting achievement is certainly the fact that we tried to estimate the amount of natural CO_2 released into the atmosphere from 1708 recorded mineral springs in Slovakia. We came to the result of 3.6 Mt/year, which is the approximate amount that produces the third largest CO_2 emitter in Slovakia - thermal power plant Nováky.

We emphasize that the work has dealt with "*selected* structures suitable for CO_2 storage" and therefore we do not assume that we have exhausted all possibilities for this purpose, which provides complicated geological setting of the Slovak territory. We have focused on structures that are close to current reality.

In addition to the above sites we address the issue of permanent CO_2 storage in suitable petrographic types of rocks. This method is not usable in every country because it requires the existence of ultramafic rocks. The results are as follows:

We have come to the finding that an unparalleled potential to absorb CO_2 have the samples of the serpentine group, where levels of magnesium component vary between 34.75 to 39.73 %. They are followed by amphibole-chlorite and talc serpentines; the least potential have the samples of the amphibolite and basalt. On average, 1 t of CO_2 could be stored in 2.6 tonnes of amorphous serpentine rocks. In the present methodology in operational stage this method of carbonatization can be suitable complement to the sites with hydrodynamic storage regimes. Its advantage is the acquisition of raw materials and contribution to improving the environment.

Thus, if in the future Slovakia plans to reduce the negative effects of climate change by CO_2 storing, the first necessary step would be a pilot project as a necessary intermediate stage prior to industrial application. In the research we have identified a number of structures - depleted hydrocarbon deposits, both in Vienna and Transcarpathian Basins, which would meet the criteria for a pilot project. The prospects of the pilot project depend on the overall situation and the need to make a step forward in that sphere.

Note: In cooperation with Nafta Bratislava a.s. we have proposed in the scope of the project CGS Europe (Czernichowski-Lauriol at al., 2010) for ZEP (Zero Effective Platform – EC advisory body) 4 sites of pilot projects (Láb, Marcelová, Ptrukša a Stretava).

However, we can conclude that, if necessary, the Slovak Republic has available appropriate structures for both the pilot as well as industry imposition of the carbon dioxide. Of course, all designed sites will require further technical work and build the infrastructure and based on the results of this forthcoming work will be possible to launch industrial CO_2 storage.

The intended technology comes to conflicts of interest mainly with the sources of mineral and geothermal waters. An important role will play economic possibilities, including fees for emissions because CCS technology is challenging not only operationally, but it is also costly. The further development will depend on the overall situation in the field of global climate change, economic and energy opportunities and the resulting political decisions. We cannot omit the public attitude, which tends to be very important input into this type of issues. Therefore, the upcoming developments will show whether the methodology of CCS in Slovakia finds practical application in the future.

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