SLOVAK GEOLOGICAL MAGAZINE

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Periodical journal of Geological Survey of Slovak Republic is a quarterly presenting the results of investigation and researches in a wide range of topics:

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- **lithology and stratigraphy**
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The journal is focused on problems of the Alpine-Carpathian region.

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Foreword

Climate change and the connected global warming count among the most frequently discussed topics of today. The 4th Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) states that 'most of the observed increase in global average temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic concentrations of greenhouse gases'. Carbon dioxide (CO_2), the most important greenhouse gas, is emitted into the atmosphere, among others, as a product of fossil fuels combustion. 80% of anthropogenic emissions of CO_2 come from big stationary point sources like power plants, steel mills, cement works or refineries.

By signing the Kyoto protocol the European Union countries committed themselves to decrease their CO_2 emissions by 8% within the 2008-2012 period, compared with the base year (usually 1990). For the next stage of the Kyoto mechanism after 2012, further cuts can be expected, starting from the 20% value. The goal to considerably decrease CO_2 emissions can be achieved using a combination of several more or less viable measures that can be divided into four main categories:

- Increasing energy efficiency of the economy and related energy savings;
- Increasing the share of renewable energy in the energy mix;
- Increasing the share of nuclear energy in the energy mix;
- CO_2 capture and storage (CCS).

According to many analyses and studies, both the world and European economies will remain dependent on fossil fuels during the next decades. Hence, it is highly probable that the CO_2 emissions will be still growing in the near future. To be able to achieve a stoppage of this growth, it is absolutely obvious that all of the four types of measures stated above will have to be applied, including CCS.

The CCS technology grounds in capture of the carbon dioxide produced by fossil fuel combustion (for power production, cement, steel, etc.), its transport to a storage site and its safe storage in deep geological structures. At present, CCS technologies are high on the agenda both worldwide and in the European Union. Clear evidences of this statement are e.g. the EC Communication "Sustainable power generation from fossil fuels: aiming for near-zero emissions from coal after 2020", envisaging massive implementation of the CCS technology in Europe in near future, or the proposal for a European Directive on the geological storage of carbon dioxide from 23 January 2008.

Implementation of the CCS technology in Europe is the main goal of the European Technology Platform on Zero-Emission Fossil Fuel Power Plants (ETP ZEP), a grouping initiated by the European Commission and associating big industrial enterprises, research & development institutions as well as environmental non-governmental organisations. Its European Flagship Programme aims at construction and operation by 2015 of up to 12 demonstration power plants equipped with the CCS technology. This should be the first stage on the way towards commercial application of CCS in Europe around 2020.

Research & development in the area of CCS was one of the priorities of 6th European Framework Programme for research, technological development and demonstration activities (FP6), as well as of its successor – FP7 - that has been launched in 2007. In new EU Member States and Associated Candidate Countries, the pioneering work was done within the CASTOR and EU GeoCapacity FP6 projects where the CO_2 geological storage potential of these countries has been assessed, in relation to the distribution of big stationary emission sources and within wide pan-European international cooperation.

On 1 October 2006, the international CO_2NET EAST project has been started, a FP6 Co-ordination Action funded by the European Commission. The main goal of the project is CCS networking extension to new EU Member States and Associate Candidate Countries. Principal project activities include building of general awareness concerning CCS technology capabilities in the countries involved as well as dissemination of knowledge and know-how coming from the main research & development projects in Europe. Project implementation is a task of a consortium consisting of 7 R&D institutions from new EU Member States and Associate Candidate Countries and StatoilHydro, the Norwegian industry partner.

This special issue of the Slovak Geological Magazine is a joint dissemination activity of CO_2NET EAST project partners and associated partners. We are grateful to our Slovak colleagues of the Dionýz Štúr State Geological Institute for enabling us to prepare this special "CO_2" issue, as well as to the European Commission and our project sponsors - Shell International Renewables, StatoilHydro, Schlumberger Carbon Services, ENEL (Main Sponsors) and ALSTOM Power, Total, Vattenfall and BP Alternative Energy (Sponsors) - for co-financing the CO_2NET EAST project and its activities.

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CO_2 geological storage and mineral trapping potential in the Baltic region

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Abstract. Estonia, Latvia and Lithuania have strong economic links and coordinated environmental policy. Furthermore, they are situated within the same geological unit, the Baltic Sedimentary cover. It urges the elaboration of the common approach in managing the CO_2 emissions, in particular as regards the geological sequestration. The smallest among three countries Estonia with 1.3 mln. population produces the highest CO_2 emissions and is among the highest CO_2 producers per capita in Europe, mainly due to oil shale used for energy production. Geological conditions in three countries are rather different, resulting in zero potential for CO_2 geological storage (CGS) in Estonia located at the shallowest part of the Baltic sedimentary basin, low CGS potential in Lithuania located at the deepest part of the basin and high CGS potential of Latvia that contains large uplifts as the potential traps for CO_2 storage. Alternative approaches are suggested for Estonia and Lithuania, focusing on the mineral trapping of CO_2. The immobilization of CO_2 by the alkaline watered ash and ash transportation water from flue gas formed by shale combustion is a prospective option in Estonia. The serpentinites abundant in the crystalline basement is a prospective media for CO_2 immobilization in Lithuania. The other option for Estonia and Lithuania is a transportation of CO_2 to the Latvian structural traps for geological storage.

Key words: industrial CO_2 emissions, CO_2 geological storage, mineral trapping, serpentinites, oil shales, ash

1. Introduction

Global annual CO_2 emissions have grown from 21 gigatonnes (Gt) in 1970 to 38 Gt in 2004 (IPCC, 2007). The measures have to be taken urgently for reduction of emissions. The carbon management consists of a broad portfolio of strategies to reduce carbon emissions via carbon capture and storage in the geological formations, enhanced efficiency of power generation and use, application of low carbon fuels and the employment of renewable energy sources (Lokhorst & Wildenborg, 2005).

According to the Kyoto protocol signed by the Baltic countries in 2002, the level of air-polluting greenhouse gases emissions should be reduced by 8% during the commitment period 2008-2012 compared to the 1990 level. Post Kyoto Targets published in a European Strategic Energy Plan "Towards a low carbon future" aimed to reduce greenhouse gas emissions by 20% to 2020 and to reduce GHG emissions by 60-80% by 2050. Compared to 1990 the greenhouse gas (GHG) emissions decreased in Baltic countries for more than 50% (Table 1). However, the changing energy market (e.g. closure of the Ignalina NPP) and increasing industrial growth urge to evaluate different options of reducing CO_2 emissions, including the assessment of the potential of geological sinks and mineral trapping. In 2006 all three Baltic countries started inventory of their CO_2 industrial sources, infrastructure and geological capacity in the framework of EU GEOCAPACITY project supported by EU Framework Programme 6 (Shogenova et al, 2007, 2008, Šliaupa et al, 2008).

The geological setting of the Baltic States is rather different from that of the other European countries that comprise a number of small sedimentary basins, while Lithuania, Latvia and Estonia are situated within one common Baltic sedimentary basin. Therefore, a joint study is required for the assessment of geological sinks. The source types and emissions differ considerably in the Baltic countries, depending on the socio-economic conditions. The main energy and CO_2 emission in Estonia comes from oil shale combustion, while CO_2 emissions in Lithuania and Latvia are significantly lower due to the utilisation of other main energy sources (nuclear and hydro-energy) and imported energy by Latvia from other countries.

Reducing CO_2 emissions using mineral sequestration involves the reaction of CO_2 with minerals to form geologically stable carbonates (Goldberg *et al*, 2000). Carbonation of the naturally occurring silicate minerals, such as serpentine and olivine, provides CO_2 storage capacity on a geological time scale. One of the advantages of this method is that magnesium and calcium carbonates are already plentiful in nature and are difficult to dissolve (Lackner & Ziock, 2000). Another option of

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mineral trapping is using of alkaline wastes, which are available in relatively large amounts and often rich in Ca and Mg. Such ash is formed during combustion of fossil fuels such as coal (Uliasz-Bochenczyk et al, 2007) and oil-shale (Kuusik et al, 2001), and also by other industries such as steel industry, municipal soild-waste incineration ashes (Costa et al, 2007), paper-produced industry ash, medical solid-waste incinerator ash (Baciocchi et al, 2006), etc. CO_2 mineral trapping by waste products could be performed ex-situ and in-situ (Geerdermann et al, 2004).

The fastest mineral carbonation process could be achieved in reactors using high temperature and pressures and concentrated CO_2. For commercial use of such reactors, mining, crushing and milling of the mineral-bearing ores and their transport to a processing plant would be required. Concentrated CO_2 stream will come to reactor from a capture plant (IPCC report, 2005). In case of the ash, reactor could be filled with the ash and alkaline transportation water collected at the same plant where CO_2 is captured. At this case process needs extra energy for reactor, but there will be no costs for ash and CO_2 transportation.

2. DISTRIBUTION AND TYPES OF STATIONARY CO_2 SOURCES

In 1990 (reference year of the Kyoto Protocol) the Baltic countries produced 48 Mt of GHG emissions in CO_2 equivalents in Lithuania, 42.6 Mt in Estonia and 26.4 Mt in Latvia. The emissions have reduced considerably since this reference year, due to large-scale socio-economic rearrangements. In 2006 these emissions were considerably lower, reduced for 56% in Latvia, 53% in Lithuania and 48.5% in Estonia compared to the amount of CO_2 in the reference year (Table 1). However, GHG emissions have increased systematically since 1999-2000 owing to economical growth (1, 3, Rimša et al, 2007). Significant increase in emissions is forecasted in Lithuania and Latvia due to the planned closure of the Ignalina NPP in 2009 and construction of new power plants using coal and gas combustion. Compared to 2005 the industrial CO_2 emissions increased by 3 Mt in Estonia in 2007.

The largest GHG emissions in the Baltic countries is produced by energy sector (Table 2), while contribution from other sectors is much less significant (1-4, Rimša et al, 2007, 2008). In 2007 twenty-two large sources exceeding 100 000 tonnes/year (Fig. 1, Table 3) produced 14.5 Mt of CO_2 in Estonia, 4.8 Mt in Lithuania and 1.9 Mt in Latvia. In Estonia CO_2 emissions per capita amounting 14.1 tonnes in 2004 are one of the highest in Europe (Table 1). For the sake of comparison it should be noted that in 2004 average CO_2 emissions per capita was 7.7 tonnes in Europe.

The high GHG emission rate in Estonia results basically from the use of oil shale for power production. Main CO_2 sources are located in the northeast of the country, close to the oil-shale deposits. The largest CO_2 sources in the Baltic countries are "Estonian" and "Baltic" electric power stations producing respectively 9.4 and 2.7 Mt of CO_2 in 2007. The Kunda Nordic cement plant produced 1.17 Mt of CO_2 in 2007 (0.746 Mt of CO_2 in 2005) (Fig.1) The other concentration of CO_2 sources occurs in the Tallinn region.

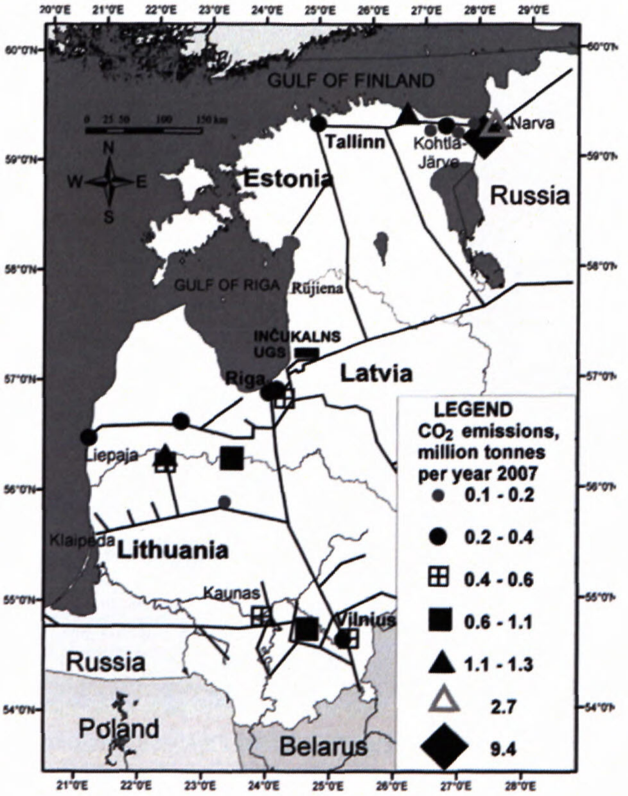

Fig. 1 Large industrial CO_2 emissions (produced in 2007) in Estonia, Latvia and Lithuania registered by European Union Emissions Trading Scheme. Solid lines show natural gas pipeline network. Rectangle shows Inčukalns underground gas storage (UGS).

In Latvia, the main CO_2 producers are located in the western part of the country. In 2007 the Liepaja metallurgical enterprise emitted 0.356 Mt of CO_2 and three electric power stations in the Riga area emitted 0.567, 0.386 and 0.23 Mt of CO_2 that is close to volumes of 2005.

There are two CO_2 source clusters in Lithuania, situated in the north-western and south-eastern part of the country. The greatest GHG producer the Mažeikiai oil refinery decreased the emissions from 1.87 Mt in 2005 to 1.20 Mt of CO_2 in 2007, while the other largest source the Akmene cement plant increased CO_2 production from 0.78 Mt in 2005 up to 1.09 Mt in 2007.

3. PROSPECTIVE CO_2 STORAGE OPTIONS

The Baltic countries are situated in the eastern part of the Baltic sedimentary basin that overlies the western periphery of the East European Craton (Fig. 2). The basin contains the Upper Vendian and all of the Phanerozoic systems as a result of protracted subsidence history. The thickness of the sediments is less than 100 m in northern Estonia, increasing to 1900 m in south-western Latvia and 2300 m in western Lithuania (Paškevičius, 1997). The Baltic basin contains several major aquifers that are viewed as prospective media for the storage of

Table 1 Total greenhouse gas (GHG) emissions and CO_2 emissions per capita.

	Total GHG emissions			CO_2 emissions per capita	
	In CO_2 equivalents, million tonnes		Reduction compared to 1990, %	Tonnes CO_2/capita	Place in world rate
Year	1990	2006		2004	
Estonia	41.6	21.4	48.6	14.1	16
Latvia	26.4	11.6	56	3.87	90
Lithuania	49.4	23.2	53	3.07	100

Table 2 Share of sectors (%) in greenhouse gas (GHG) emissions in countries.

Emissions	Estonia	Latvia	Lithuania
Energy (fuel combustion and emissions from fuels in all sectors, including transport) Fuel combustion in transport	89 10	72 27.5	58 18.2
Agriculture	5.7	17.7	17.9
Industrial processes	2.7	2.5	16.6
Waste	2.5	7	6.8

Table 3 CO_2 emissions registered in European Union Emission Trading System (EU ETS).

Large CO_2 sources(>100 thousand tonnes) registered in EU ETS						
	Million tonnes	Number of sources	Share in ETS emissions, %	Million tonnes	Number of source	Share in ETS emissions, %
Year	2005			2007		
Estonia	11.5	9	91.3	14.5	9	94.6
Latvia	1.9	6	63.8	1.9	5	65.7
Lithuania	5.6	9	84.8	4.8	8	80.0

All registered in EU ETS industrial sources

	CO_2 emissions, million tonnes	Number of sources of verified emissions	EU ETS share in total GHG emissions	CO_2 emissions, million tonnes	Number of sources of verified emissions
Year	2005			2007	
Estonia	12.6	41	59.3	15.3	47
Latvia	2.98	89	26.7	2.89	89
Lithuania	6.6	89	32.5	6	93

CO_2. However, a prospective media should meet certain requirements, among which the most important are the large volume of the reservoir, suitable depth and temperature, and presence of a reliable seal (including structural tightness). Neither coal nor salt deposits are present in the sedimentary cover.

Deep saline aquifers are by far the most accepted proposal for large-scale CO_2 storage. The high water salinity renders these layers unsuitable for use as drinking water or for watering plants. Depending on the formation pressure and temperature, CO_2 can be stored either as high-density gas phase or in a supercritical state ($P > 73.8$ bars, $T > 31^{\circ}C$).

The Baltic basin contains also a number of oil fields related to Cambrian siliciclastic and Ordovician and Silurian carbonaceous reservoirs. Therefore, the storage of CO_2 in the depleted oilfields and the EOR option are considered as the potential technology in the Baltic area.

Oil fields are exploited in west Lithuania, Kaliningrad District and offshore Poland. In Lithuania, oil fields

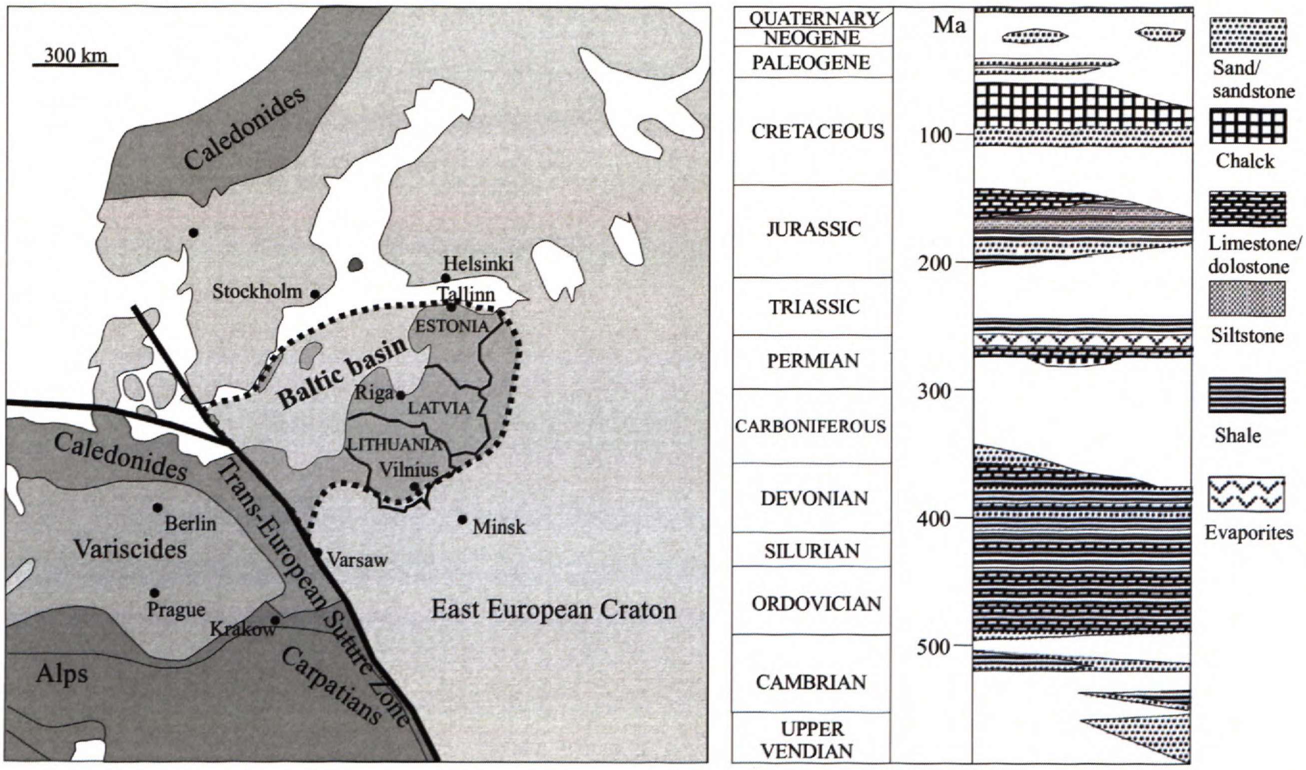

Fig. 2 Geological setting of the Baltic sedimentary basin (basement tectonic sketch map, modified after EUROPROBE TESZ Project).

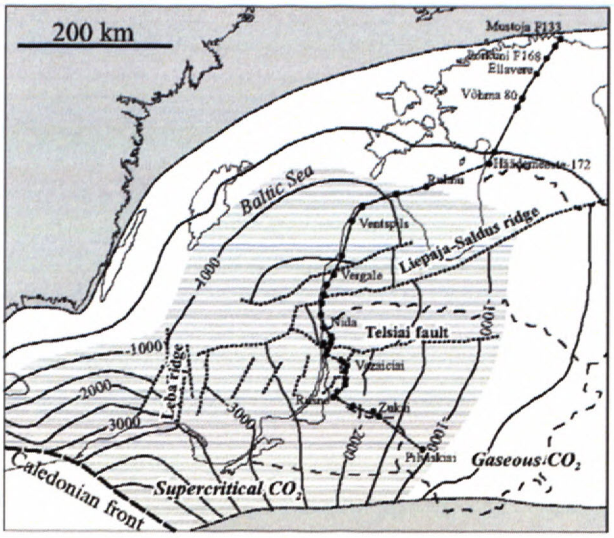

Fig. 3 Depths of top of Cambrian aquifer. The contour lines indicate the depth of the top of Cambrian. The hatched lines show major faults. The P-T fields of gaseous (white) and supercritical (dotted) state of CO_2 are indicated. The line of the geological cross-section shown in Fig. 3 is indicated.

are confined to two major tectonic zones, i.e. the Telšiai fault zone and the Gargždai fault zone. Some oil shows (and a small Kuldiga oil field) were discovered in Cambrian and Ordovician reservoirs in Latvia (Brangulis et al, 1992). The Silurian reefs contain small oil fields in Central Lithuania, which are not exploited.

In Lithuania, 15 oil fields are presently exploited. The size of oil fields ranges from 16,000 to 1,400,000 tonnes of the recoverable oil. The storage potential of the largest oil fields of west Lithuania does not exceed 2 Mt of CO_2, with the total storage potential estimated to be around 7 Mt of CO_2, which is just a little more than the annual stationary CO_2 emissions of the country (Sliaupa et al., 2008).

Another option is the utilisation of carbon dioxide for enhancement of the oil recovery (Crawford et al., 1963). Most of the oil fields have reached the tail phase and EOR can prolong the lifetime of those oil fields. The oil is light and exceeds 35 API° *(Zdanavičiūtė, O., Sakalauskas, 2001)* meaning that CO_2 could be injected in miscible conditions - a favourable factor for CO_2 sequestration. The estimated total EOR net volume of CO_2 is 5.7 Mt (Sliaupa et al., 2008).

4. DEEP SALINE AQUIFERS

4.1. Potential aquifers

Only two large aquifers of the Baltic sedimentary basin meet requirements listed above, i.e. the Lower-Middle Devonian (Pärnu-Kemeri formations) and Middle Cambrian aquifers buried to depths exceeding 800 m (Fig. 3-5).

The Cambrian reservoir is distributed in all Baltic countries. The depth varies from outcrops in Estonia to more than 2 km in west Lithuania (Fig. 3, 4). The depth of the reservoir exceeds 800 m in west Latvia, west Lithuania, north Poland, and in the Baltic offshore, while the aquifer beneath Estonia is shallower than the limit of the supercritical state of CO_2. The reservoir is composed of quartz sandstones with subordinate siltstones and shales. The thickness of the aquifer is in the range of

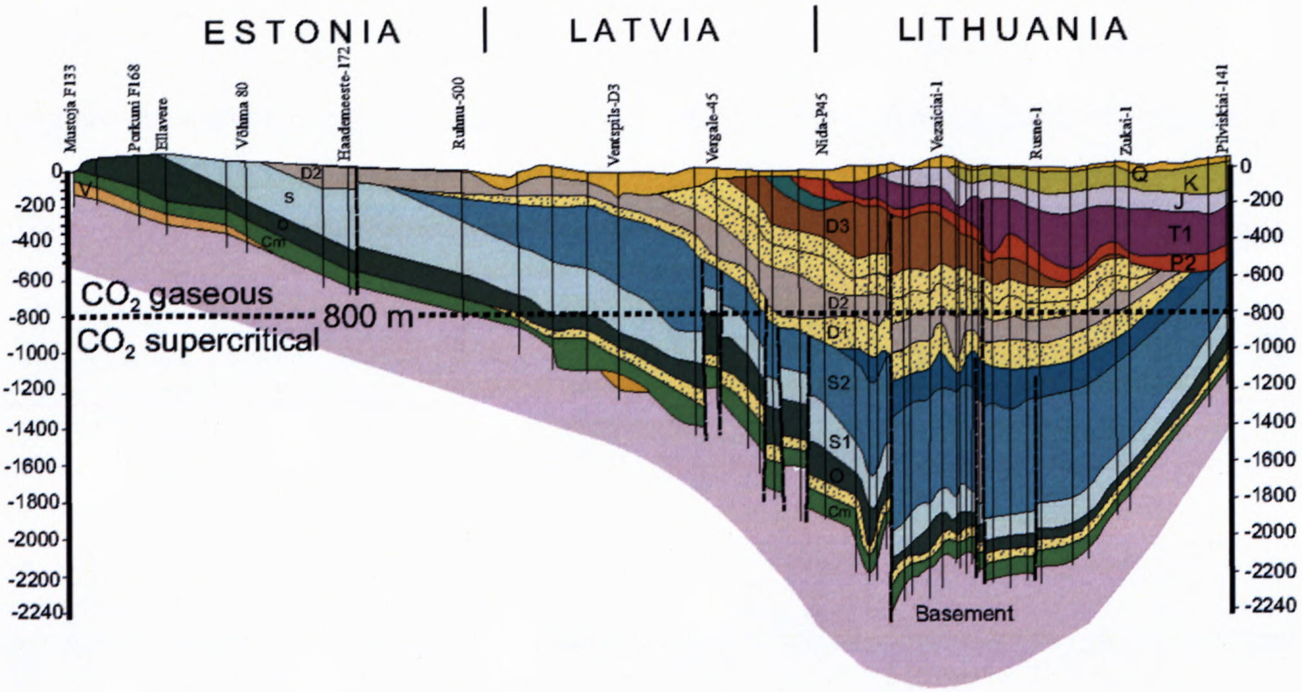

Fig. 4 Geological cross-section across Estonia, Latvia, and Lithuania. Major aquifers are indicated by dots. V – Vendian (Ediacaran), Cm- Cambrian, O – Ordovician, S – Silurian, D1, D2 and D3 – Lower, Middle and Upper Devonian, P2 – Middle Permian, T1 – Lower Triassic, J – Jurassic, K – Cretaceous, Q – Quaternary.

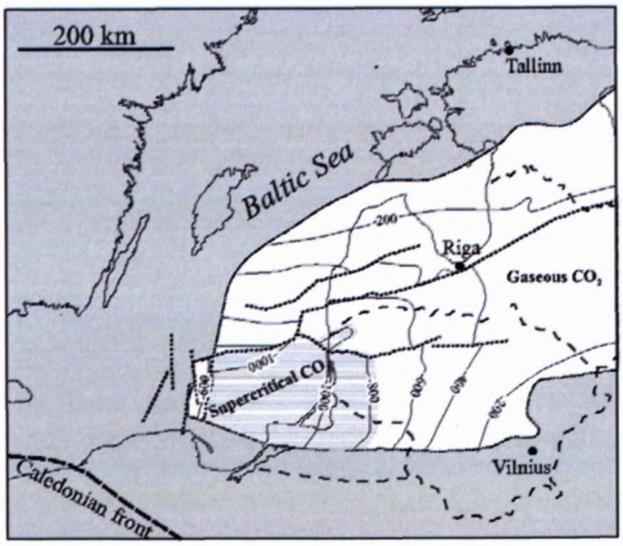

Fig. 5 Depths of top of Pärnu-Kemeri aquifer. The contour lines indicate the depth of the top of Devonian. The hatched lines show major faults. The P-T fields of gaseous (white) and supercritical (dotted) state of CO_2 are indicated.

20-70 m. Due to considerable variations in depth and temperature, the porosity of sandstones changes dramatically across the basin, from 20-30% in the northern and eastern shallow part of the basin to less than 5% in the central and western parts of the basin (Šliaupa et al, 2003). The Middle Cambrian aquifer is sealed by a 500-900 m thick Ordovician-Silurian shale caprock.

The Pärnu-Kemeri aquifer lies in the central part of the basin (Fig. 5). Its depth exceeds 800 m in west Lithuania and the south-eastern part of the Baltic Sea. The aquifer is composed of arkosic sandstones containing 20–37% of siltstone and shale layers (Šliaupa et al, 2005). Average porosity of sandstones is 26%; permeability is in the range of 0.5–4 D. Total thickness of the aquifer varies from 100 to 160 m in west Lithuania. The aquifer is covered by 80–120 m thick marlstones attributed to the Narva Formation constituting a basin-scale aquitard.

Upon injection into saline aquifers, carbon dioxide may be stored by (1) hydrodynamic (structural) trapping, (2) solubility trapping (carbon dioxide dissolved in aquifer water), (3) residual trapping, and (4) mineral trapping. Solubility and mineral trapping are the most important long-term solutions to carbon dioxide sequestration in geological media. However, these processes involve larger proportion of injected CO_2 only 100 years after the injection, whereas hydrodynamic trapping becomes effective immediately and can be compared to existing natural analogues.

4.2. Structural trapping potential

Sixteen major structures, with estimated storage capacity 5.4–58.3 Mt CO_2, have been identified in west Latvia (Fig.6, Geological Structures, 2007), while only small-scale uplifts were identified in Lithuania (Šliaupa et al, 2005). The storage capacity of a structural trap was estimated:

$$M_{CO2} = A \times h \times \varphi \times \rho_{CO2r} \times S,$$

where M_{CO2} is the storage capacity (kg), A is the area of a closure (m), h is the net thickness of reservoir sandstones (m) (typically is 20-40 m in Latvia and Lithuania), φ is

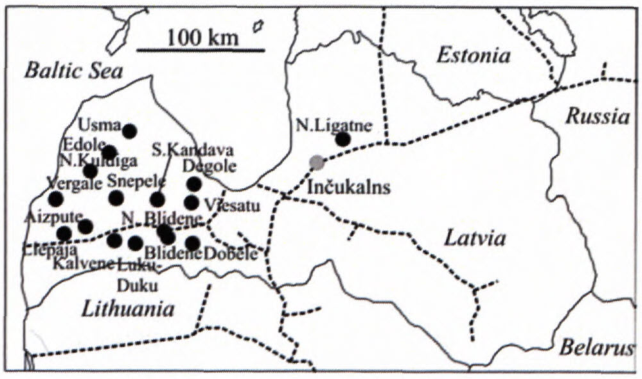

Fig. 6. Major Cambrian aquifer structures (CO_2 storage potential exceeding 10Mt) of Latvia (black circles) and Inčukalns underground gas storage (grey circle). Hatched line shows gas pipelines.

the porosity (typically ranges from 0.25-0.20 in central Latvia and central Lithuania to 0.06 in west Lithuania), ρ_{CO2r} is the in situ CO_2 density at reservoir conditions (ranges from 600 kg/m^3 in west Lithuania to 750 kg/m^3 in central Lithuania and central Latvia), S is the sweeping efficiency, often also referred to as the storage efficiency (assumed 0.35, taking into consideration very large size of the aquifer and proved high storage efficiency of the Inčukalns underground gas storage in Latvia operating since 1968).

The total capacity of 16 large structures of Latvia is conservatively estimated as 404 Mt of CO_2, with the potential of the greatest uplifts 40–60 Mt of CO_2, and even more using optimistic estimation of storage potential. The depths range from 650 to 1200 m. The thickness of Cambrian reservoir rock represented by sandstone is 40-60 m, average porosity 22%, permeability 3-7 Darcy. The structures are similar to the Inčukalns underground gas storage. The total volume of UGS was estimated as 5.7 billion m^3, from which 4.46 billion m^3 is filled now by natural gas (Geological Sructures, 2007).

The major CO_2 emitting sources of Latvia are located close to major uplifts. Furthermore, the CO_2 sources and potential traps are located close to the existing gas supply pipelines, which potentially reduce the cost of CO_2 transportation.

The capacities of more than 100 Cambrian local uplifts identified in Lithuania were evaluated recently (Šliaupa et al, 2005). The two largest Vaskai and Syderiai aquifer structures can store only 8.7 and 21 Mt of CO_2, respectively, while the rest structures are of much lesser volume. Therefore, the hydrodynamic trapping in Cambrian aquifer structures has very limited prospects in Lithuania.

No structural traps have been identified in the Pärnu-Kemeri aquifer, neither in Lithuania nor in Latvia due to low-intensity tectonic deformation of the Variscan structural complex (Stirpeika, 1999).

4.3. Solubility trapping

The solubility trapping is not restricted to particular structures. The solubility of CO_2 ranges from 2% to 6%, depending on the brine salinity, temperature, and pressure (Bachu & Adams, 2003). However, the large volume of a regional-scale aquifer provides an attractive alternative for CO_2 disposal. The solution time is of order of 10^2-10^3 years, which is considerably longer than the hydrodynamic trapping process (Ennis-King et al, 2003). Before dissolving, the CO_2 phase migrates towards the basin margins, which may cause the risk of gas escape either through the faults or shallow margins of the basin. Therefore, the safe distance of gas migration should be evaluated before selecting prospective sites for CO_2 injection.

The solubility trapping potential has been calculated using the approach presented in (Bachu & Adams, 2003). It accounts for the brine salinity, temperature, pressure and reservoir properties that vary considerably across the Baltic basin. The solubility of CO_2 in Cambrian formation water varies from 25–30 kg/m^3 in west Lithuania to 40–50 kg/m^3 in east Lithuania and Latvia (Table 4). The CO_2 storage potential changes westwards from 0.4 Mt/km^2 to 0.05 Mt/km^2. The calculated total solubility trapping capacity is as high as 11 Gt of CO_2 within the area of the supercritical state of the carbon dioxide.

Table 4. Solubility trapping in Cambrian reservoir in west, central, and east Lithuania

Parameters	West Lithuania	Central Lithuania	East Lithuania
Aquifer temperature, °C	75	55	40
Aquifer Pressure, MPa	20	15	10
Salinity, g/l	160	110	90
CO_2 solubility, kg/m^3	28.1	35.6	40.9
Effective thickness, m	20	35	40
Porosity, %	10	20	25
Solubility storage in 1 km^2 area, Mt of CO_2	**0.056**	**0.249**	**0.409**

The Pärnu-Kemeri aquifer is characterised by better reservoir properties, but has a smaller area of extent than the Middle Cambrian reservoir. CO_2 solubility ranges from 36 kg/m^3 in the deep part of the basin to 60 kg/m^3 in the shallow periphery of the basin. In west Lithuania the storage capacity of the reservoir is about 1 Mt of CO_2 in 1 km^2 area. The total onshore potential of this formation is estimated as high as 1 Gt of CO_2.

5. MINERAL TRAPPING

5.1. Mineral trapping in aquifers

The mineral trapping that involves a series of interactions between the formation mineralogy and CO_2-enriched aquifer waters, can convert CO_2 to carbonate, an immobile and harmless mineral that will be stored for millions to hundreds of millions of years (Bruant et al, 2002). Reactions with Ca/Mg/Fe-bearing silicate minerals are the most promising for carbon sequestration because these silicates neutralize the added acidic CO_2 and provide alkali metals that trap CO_2 through the precipitation of carbonate (Gunter et al, 1997). These reactions can be summarized as follows (Hitchon 1996): Ca/Mg/Fe feldspar + clays + CO_2 + H_2O = kaolinite + Ca/Mg/Fe carbonate + quartz.

The Middle Cambrian reservoir comprises quartz sandstones that are practically not reactive to carbon dioxide. The Pärnu-Kemeri sandstones contain clay admixture (up to 10%) and feldspar grains (up to 15%). Therefore they have a potential for permanent immobilisation of carbon dioxide in mineral form. Assuming the rock capacity of 10 kg/m^3 (Bachu & Adams, 2003), the sequestration potential can be evaluated to reach 5.6 Gt of CO_2 (onshore). Taking into consideration injection limitations the realistic number would be an order lower.

5.2 Mineral trapping in ultramafic rocks

The ultramafic rocks have been identified as the most suitable rock media for mineral trapping of carbon dioxide. However, they are rather rare and can provide only the limited reserves for CO_2 sequestration. Alternatively, the serpentinite rocks are abundant in the world and can serve for immobilization of CO_2. The large serpentinite province was mapped in the Palaeoproterozoic crystalline basement of south Lithuania. Serpentinites associate with the high-quality iron ore that provides the opportunity for the cascade utilization of these formations. Serpentinites are distributed in the southeastern part of the Lithuania in the Varena Geological Province (Figure 7). More than a dozen of serpentinite bodies were identified in south Lithuania. Owing to their association with the iron ore deposits these bodies were extensively studied by the drilling. They subcrop at the top of the basement and are covered by the platform sediments of 280-500 m thickness. With respect to the major CO_2 emission sources the Varena Serpentinite Province is located close to the south-eastern cluster of emission sources, the distance to the particular sources varying from 50 km to 150 km.

The carbon dioxide is immobilized by reacting with the serpentinite to form stable minerals. The serpentinite represent the by-product of the iron ore exploitation. It is important that the most of the technological chain used for the magnetite extraction is applied in CO_2 carbonation procedure that is as following: *Serpentine → Crushing → Grinding → Screening → Magnetic separation (iron ore* Fe_3O_4*) → Reactor (*CO_2*, solution).* Only the last operation in this chain is applicable for just the carbonation of the serpentine.

Roughly, the ratio of the immobilized CO_2 to the serpentinite is assumed 1:2. The volume of the serpentinites in the largest Varena Iron Ore Deposit is estimated 1-2 Gt. Consequently, the sequestration potential is evaluated as high as 0.5-1 Gt. It equals to CO_2 production during 200-500 years in the south-eastern CO_2 emission cluster. The other serpentinite bodies identified in southeast Lithuania are much smaller. Assuming the total capacity of the rest objects at least equal to the Varena Iron Ore Deposit, they provide considerable potential for mineral sequestration of the carbon dioxide.

5.3. Mineral trapping by oil shale ash

The technology of CO_2 mineral trapping with waste oil shale ash is under development in Republic of Estonia. The concept for abatement of CO_2 emissions in power production based on oil shale ash as sorbent for CO_2 mineralization has been proposed and elaborated (Figure 8). State funded investigations of Tallinn University of Technology, thereby within the framework of Nordic-Baltic project NoCO$_2$ and under support of energy sector as well as of Ministry of Environment of Estonia shows that the amount of CO_2 which is possible to bind with oil shale ash can cover about 10-12% of the total industrial CO_2 emissions in Estonia (Kuusik et al, 2001,2002a, 2002b, Uibu & Kuusik 2007, Uibu et al, 2007, 2008, 2009).

Estonian oil shale is a carbonaceous fine-grained sedimentary rock of Ordovician age with 10-60% of kerogen (solid organic matter), high carbonate content (20-70%) represented by limestone, or more rarely by dolomite, and 15-60% of siliciclastic minerals (sandy-clay). As a fuel oil shale has a low net calorific value (8-9 MJ/kg). During combustion of one tonne of oil shale 450 kg of ash is produced. In case of mineral coal only 100 kg of ash is produced. Thereafter oil shale is a low-grade fuel.

Oil-shale is produced in two qualities: with grain size of 0-25mm and 25-125 mm. The enriched lumpy oil shale (25-125 mm) with higher calorific value is used to produce shale oil and as fuel in cement kilns. About 77% of the mined oil shale (grain size 0-25 mm) with lower calorific value is used as boiler fuel in large power plants. During combustion of powdered oil shale CO_2 is formed not only as a burning product of organic carbon, but also as a decomposition product of the ash carbonate part. Therefore the total quantity of carbon dioxide increases up to 25% in flue gases of oil-shale (1).

Oil shale ash contains up to 20-25% free Ca-Mg oxides. Portlandite $Ca(OH)_2$ forming from free lime during hydraulic transportation and wet deposition of ash can bind CO_2 also from air. Natural weathering process could be accelerated by simple methods. It has been demonstrated by batch and continuous mode experiments that by processing of the ash – water suspension by flue gases the CO_2 binding ability of ash could be utilized completely. The results of these experiments show that watered oil shale ash can bind 80-160 kg and more of CO_2 per one tonne of ash, and 30-80 kg CO_2 could be bound by alkaline wastewater used for transportation of one tonne of ash (Uibu, Kuusik, 2007).

From annual production of about 14 mln tonnes of oil shale in Estonia, 10,8 mln t (77%) are the share of oil shale combustion by Energy Sector. Taking into account that 450 kg of ash is produced from every one tonne of combusted oil shale, about 5 mln tonnes of ash are produced annually. The amount of CO_2 bound by oil shale ash in wet mineralization process by flue gas could reach 400 – 800 thousand tones and by alkaline wastewater neutralization process in reactor 150– 400 thousand tonnes. The maximum amount of CO_2 bound with flue gas could be summarized as

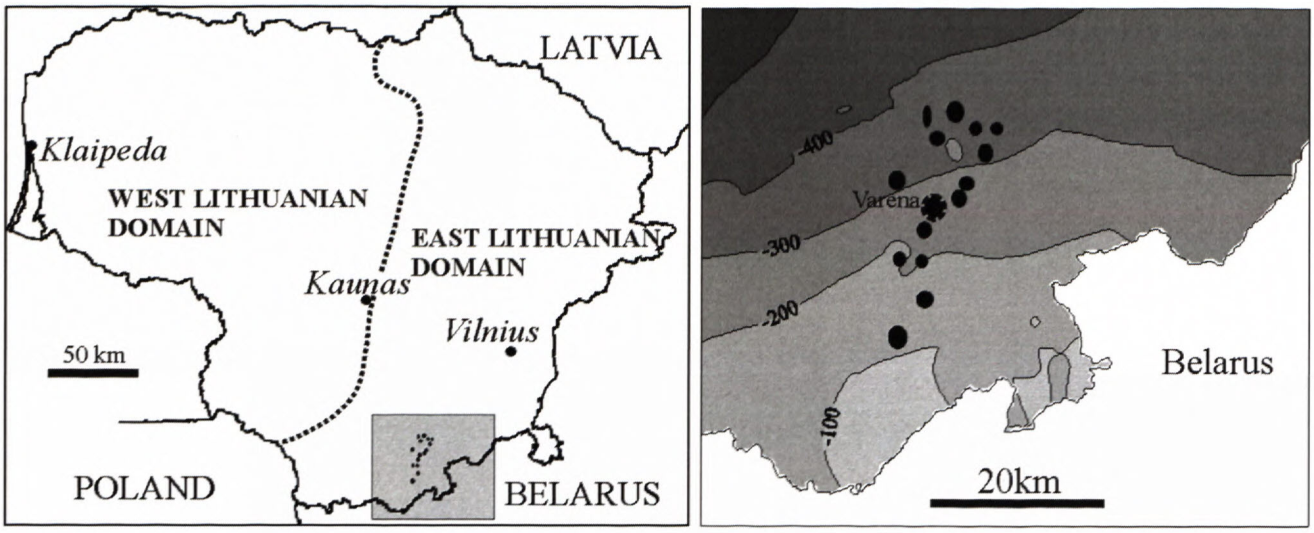

Fig. 7 Left figure shows major lithotectonic domains of the crystalline basement of Lithuania. The Varena Geological Province is shaded. Right figure zooms in the Varena Geological Province. The Varena Iron Ore deposit is distinguished. The depths of the top of the crystalline basement are indicated.

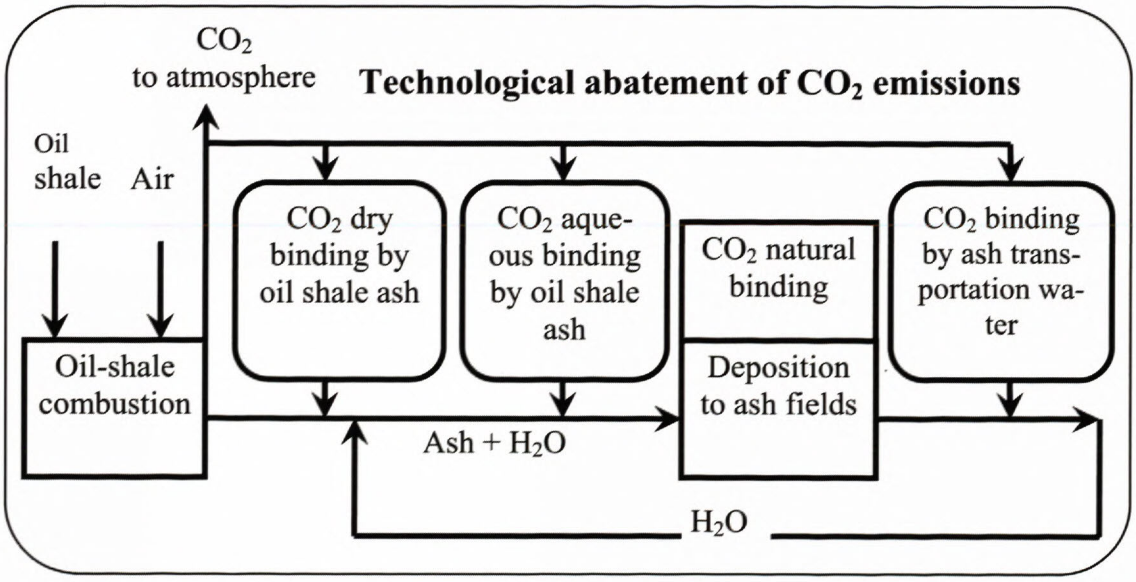

Fig. 8 Concept for CO_2 binding in oil shale-based power production

550 – 1200 thousand tonnes. Taking into account that big industrial Energy enterprises using mainly oil shale produced 11.5 million tonnes CO_2 in 2005, the maximum ratio of CO2 which is possible to bind with oil shale ash and transportation water by flue gas could estimated as 10-11% of CO_2 emitted.

The further studies with concentrated CO_2 could increase these numbers but not dramatically. Performed experiments with flue gas already showed that CaO was bound up to 100% and increase could give only MgO and Ca-silicates which showed binding degree 37-89% (Uibu et al, 2007, Uibu & Kuusik 2007). There exist some prerequisites that carbonates formed as result of the binding process could be separated and used as independent by-product, but more useful is to store them in the closed oil-shale mines. The last solution will permit to fill underground mining cavities and to prevent environmental problems arising from ash heaps.

6. Conclusion

CO_2 sources are distributed unevenly in the Baltic countries and the types of CO_2 sources vary considerably. Major emissions are concentrated in the coastal area of the Gulf of Finland in Estonia. Due to the utilisation of oil shale for energy production, CO_2 emissions produced by two largest Estonian power plants (12.1 Mt in 2007) exceed the CO_2 produced by all of the Lithuanian (6 Mt) and Latvian (2.89 Mt) stationary sources. During 2007 CO_2 emissions from Estonian industrial sources increased by about 18% mainly owing to increased energy production of these two power plants largest in the region.

Baltic countries are situated within the Baltic sedimentary basin. Two prospective aquifers of the Lower-Middle Devonian and Middle Cambrian meet the basic requirements for CO_2 storage. However, only Latvia contains structural traps large enough to store the industrial

CO_2 emissions. The capacity of 15 large uplifts have the total capacity exceeding 300 Mt that amounts to more than 150 years of country's CO_2 stationary emissions.

As for Lithuania and Estonia, the transportation of CO_2 to Latvian storage site can be a potential option, which, however, may meet serious political and public opinion problems. The alternative approaches should be therefore considered. The in-situ solubility and mineral trapping in the deep saline aquifers are still long-term technologies to develop (McGrail et al., 2001).

The mineral trapping of CO_2 from flue gas with alkaline ash produced by oil shale combustion and ash transportation water could bind up to 10-12% of industrial CO_2 emissions in Estonia. Application of this technology can solve several environmental problems in Estonia: decrease of CO_2 emissions and ash residues, filling of the closed oil-shale mines with produced minerals and decreasing the risk of the surface crashing, saving of natural landscape, etc.

In Lithuania, the prospective formation for the mineral trapping is represented by serenities located in the crystalline basement of the south of the country where the basement is covered by only thin sedimentary cover. Still, the technologies are immature and need further developments.

Acknowledgment

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CO_2 contents in soil air for needs of carbon dioxide storage monitoring

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Abstract. There have been conducted an investigation on CO_2 concentration in soil air in the Jastrzabka Stara oil reservoir area, the Carpathian Foredeep in SE Poland, in 2006 - 2007. The reservoir was selected as location of a research CO_2 injection installation. Monitoring procedures were executed to define background of CO_2 concentration in soil air before injection starts.

Measurements were performed at 24 sampling points located in the SE part of the reservoir, basing on a methodology described in the paper.

Measured CO_2 concentration values in the covered area range from 1 to over 5 %. There has been observed a concentration variability depending on sampling point location or seasons. The least concentration was measured in autumn, a bit higher was measured in springtime, both were below 2 % (majority were below 1 %).

The highest CO_2 concentrations were logged in summer time, measured concentration values exceeded 5 %. Measurement results display variability of CO_2 concentration in soil caused by seasonal biological activity and other natural factors.

They reveal usefulness of further measurements allowing CO_2 concentration background estimation in soil air, as reference in underground CO_2 injection monitoring procedures.

Key words: monitoring, storage, carbon dioxide, soil air measurement

Introduction

Carbon dioxide geological sequestration requires appropriate monitoring methods proving that the process is run safely and in an effective way. CO_2 storage monitoring is performed using various methods: direct (geochemical methods) or indirect (geophysical techniques and other) (Tarkowski et al., 2005).

These techniques allow to register dynamic processes combined with CO_2 downhole injection. They are borrowed from: petroleum industry (natural gas storage systems), know-how on hazardous and liquid waste storage in geological formations, underground hydromonitoring, ecosystem research and other (Benson & Myer, 2002; Benson et al. 2002, 2002a).

Direct CO_2 concentration measurements in water or ground/soil air make an essential part of the monitoring procedures. It allows to register CO_2 concentration in near subsurface ground layers, soil, surface and underground water, injection well vicinity, abandoned boreholes (Strutt et al., 2002).

One of methods used to examine both underground sink and CO_2 injection facility tightness is monitoring CO_2 concentration in ground subsurface. Atmogeochemical methods hither applied allow to directly detect CO_2 in ground air, being both reliable and inexpensive, as well as devices applied being easy to transport and operate.

The results allow to read gas level changes in soil air and to estimate migration tendencies. Majority of techniques applied to CO_2 concentration measurement in ground air is based on IR radiation absorbance by that gas. There are two basic types of these apparatuses: non-dispersive IR gas analysers (NSDIRs) and IR diode laser instruments (Monitoring … 2005; Pearce et al., 2005).

The paper presents preliminary measurement results of CO_2 contents in soil air in the area of an almost exhausted oil reservoir - the Jastrzabka Stara (Tarnów region, SE Poland). It was chosen as location for an underground CO_2 injection research installation (The in-situ researches ..., 2006; Tarkowski, 2007).

Carbon dioxide storage monitoring is to be examined in the location (first three years of CO_2 injection operation), combined with estimation of oil recovery enhancement prospects for the reservoir (CO2-EOR response examination). The results displayed cover initial stage of CO_2 underground storage monitoring, that is background estimation of ground air CO_2 contents.

The measurements started in 2005 and will be run next years (Introductory research…, 2005). The read background will be used as reference in CO_2 storage operation monitoring, during injection process as well as afterwards. The gas concentration increase could suggest that there is a CO_2 seepage.

1. The location and reservoir geology

The Jastrzabka Stara oil reservoir is located in SE Poland, in the Podkarpackie Voivodeship area, within commune of Czarna, 35 kilometers NE from Tarnów. Morphology of the reservoir area is hardly diversed. Rural landscape is filled with scattered buildings, mellow hills, farmlands and green meadows, and the terrain absolute altitude range from 210 do 255 m above see level.

State Geological Institute of Dionyz Stur, Dionyz Stur Publisher, Bratislava 2009

Table 1 Combination of CO_2 concentration measurement results (%) for given time intervals

Well number	5 min	20 min	30 min	60 min	120 min	240 min	360 min	480 min
1	1.34	1.68	1.78	1.85	1.81	1.89	1.87	1.84
2	1.34	1.6	1.73	1.73	1.7	1.81	1.75	1.73
3	1.87	1.79	1.95	1.9	1.9	2.13	2.11	2.02
4	1.62	1.89	1.82	1.93	2	2.04	2.04	2.02

The reservoir is located in the Carpathian Foredeep that is filled up with autochtonic Miocene sediments, lying on a bedrock formed of Jurassic and Cretaceous rocks. Within the Upper Jurrasic formations, in calciferous-marls Senonian complex, occur three sandstone reservoir levels bared with hydrocarbon accumulation.

The reservoir is tightened by younger Jurrasic strata in the central part, the peripherals being eroded and therefore tightened by Tertiary rocks. Hydrocarbon accumulation in the area of Jastrzabka Stara oil reservoir is combined with an anticline structure of NW-SE length. Nowadays seven wells (Jastrzabka Stara 6, 7, 8, 12, 15, 20 and 21) are operational there and produce oil.

2. Ground air CO_2 concentration measurement methodology

Ground air CO_2 concentration measurements were performed in SE part of the reservoir, within area around and between JSt-12 and JSt-8 wells that are 1 200 m distant each other. The JSt-12 well is selected to be an injection well while the least distant neighbouring well (JSt-8) is chosen to be the monitoring one (The in-situ researches...., 2006; Tarkowski, 2007).

In the area there were defined 24 sampling points. The point grid definition is combined with CO_2 injection prospects, therefore likely closest seepage locations. The sampling points are defined in farmlands and meadows, ground there occurring is sandy, sometimes sand loamy.

Measurements of CO_2 contents in ground air consisted in:

- sampling point tracking down by a GPS device
- hole of 4 cm diameter boring down to 80 cm depth with a hand-driven sounder
- the borehole insulation from atmospheric air by plugging
- measurement of soil air CO_2 concentration at bottom of the borehole, after at least 2 hours, using a gas sounder and a MultiRaePlus IR detector of maximum CO_2 threshold of 5 %.

The time gap between sampling borehole drilling and measurement was determined experimentally (Tab.1). There were performed about 160 measurements of CO_2 contents in these sampling points, in springtime, summer and winter season in 2006-2007. In some cases measurement was not possible due to borehole inundation during the time gap or some other reason.

3. Results of CO_2 concentration measurements

Results of ground air CO_2 concentration measurements are displayed in diagrams (Figs. 1 - 3). They display gas concentration changes at the sampling points in different seasons.

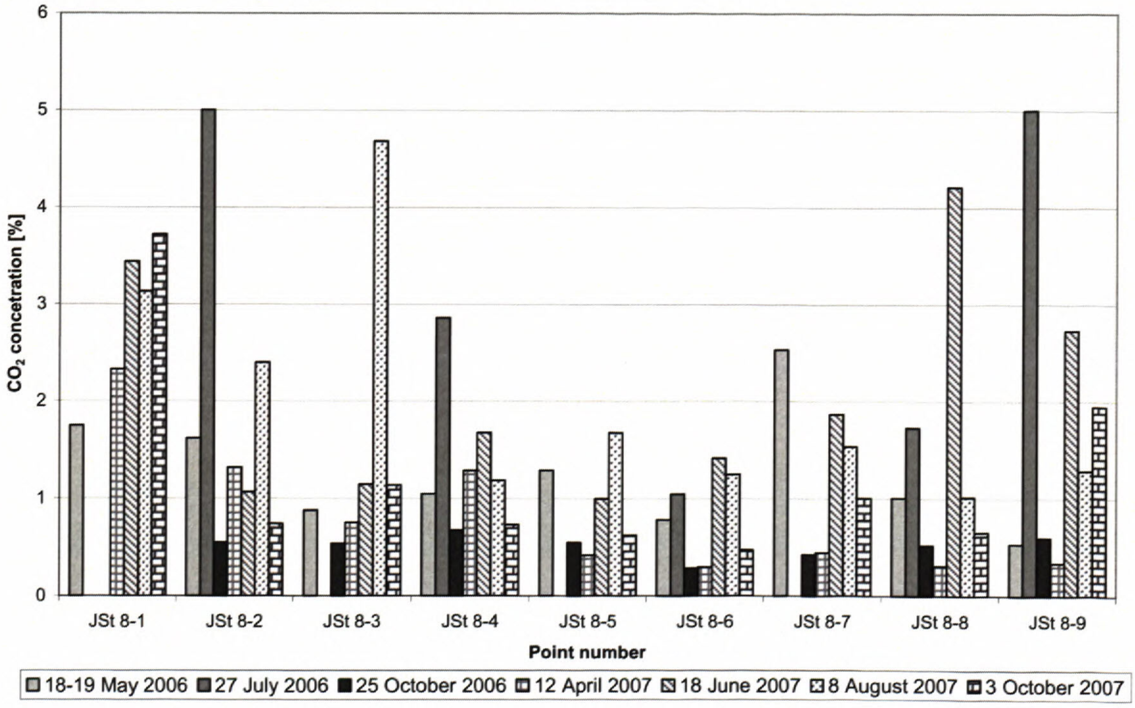

Fig. 1 Soil air CO_2 concentration around the JSt-8 production well in the Jastrzabka Stara reservoir area (2006-2007)

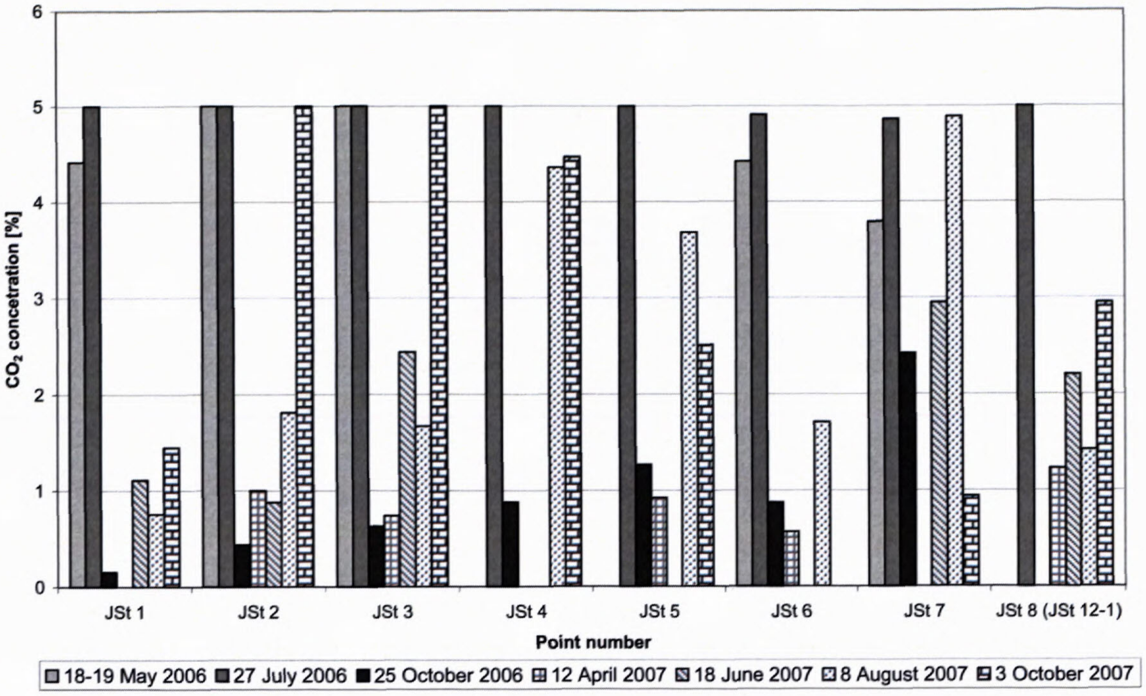

Fig. 2 Soil air CO_2 concentration by a lane between JSt-8 and JSt-12 production wells in the Jastrzabka Stara reservoir area (2006-2007)

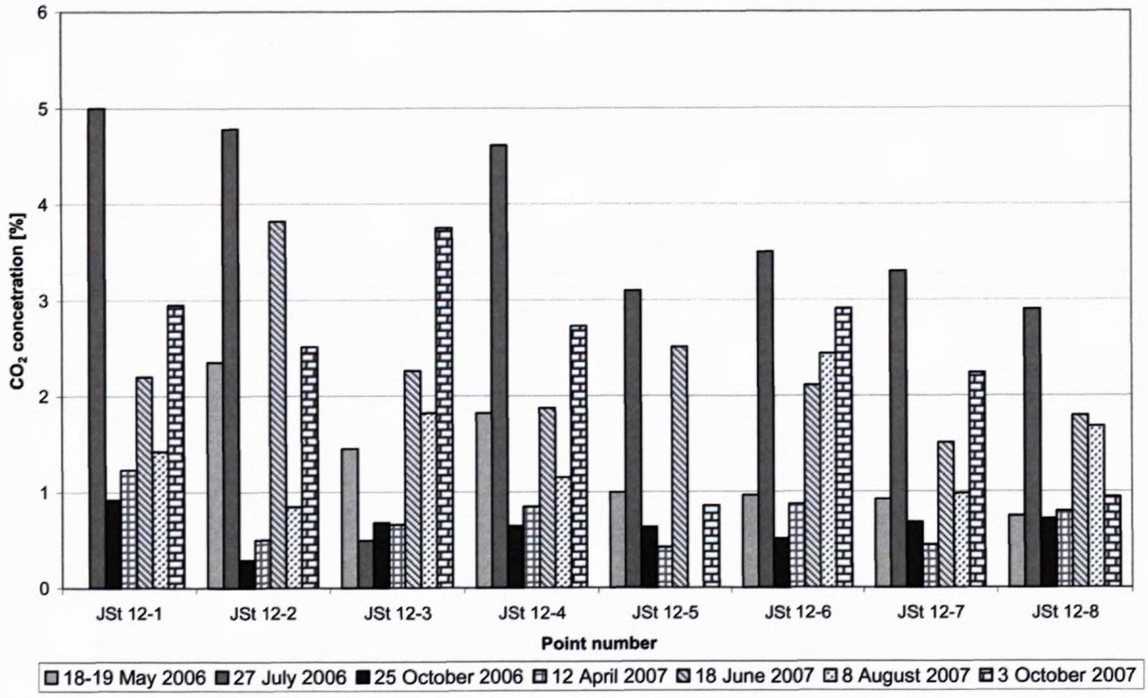

Fig. 3 Soil air CO_2 concentration around the JSt-12 production well in the Jastrzabka Stara reservoir area (2006-2007)

For the investigation period measured CO_2 concentrations have only thrice exceeded 5 % in the JSt-8 well vicinity, in JSt 8-2, JSt 8-7, JSt 8-9 sampling points, all in July. It has been remarked that measured CO_2 concentrations in all sample points are generally similar to each other for a given month of investigation. Anomalous, elevated CO_2 concentration appear in the JSt 8-1 sampling point located by the JSt-8 well. However it is obvious that in April and October CO_2 concentration was the least.

CO_2 concentration measurement results measured between JSt-8 and JSt-12 production wells (Fig. 2) are far higher than those obtained for sampling points around the wells. For a dozen of points concentration reaches or exceeds 5 %, in summertime (July, August). In early springtime and late autumn observed CO_2 concentrations were the least.

Carbon dioxide concentration around the JSt-12 production well (Fig. 3) has only twice exceeded 5 % for investigation period, in JSt 12-1 and JSt 12-5 sampling points, just in summer months (July, August). High stability of measurement results is observed for springtime and autumn months when concentration does not exceed 2 % and usually is below 1 %.

The results obtained so far display clear impact of cycle of the seasons on the CO_2 concentration in CO_2 in ground air. The gas concentration clearly depend on the season when measurements took place. The dependence read from results having been obtained for the last two years follows such outline: July (the highest concentrations observed) < June< August< May< April< October (the least concentrations observed).

Variable weather conditions (air temperature) and flora activity probably impact results the most, considering such factors as soil humidity and fertility as well.

It has been perceived that high CO_2 contents variability in the investigated area might be impacted some other way. Possible impact factors might be natural like: geological structure, kind of local bed and ground, terrain morphology (the JSt- 8 production well is situated higher – 243 m above see level while the JSt- 12 production well is situated lower – 229 m above see level).

It is to stress that read CO_2 concentrations in ground air are much higher than those observed in other areas (Ciężkowski et al., 2002).

Conclusions

Obtained results display the first, interesting image of the CO_2 concentration diversity in ground air being impacted by cycle of the seasons and natural environmental conditionings. These results indicate purposefulness of further investigations, run also in winter (regarding mild winters), as well as they indicate necessity to observe various parameters that might impact measurement results. Longer investigations would allow to read ground air CO_2 concentration background more reliably as a reference for the gas underground injection and storage process monitoring.

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CO_2 sequestration with the use of fly ash from hard coal and lignite combustion

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Abstract. Mineral sequestration relies upon permanent CO_2 bonding in natural minerals or wastes. It is an ecologically safe method, because CO_2 is permanently bonded, and the occuring in the reaction carbonates do not affect the environment negatively. For CO_2 bonding there may be used natural mineral resources such as f.ex.: olivines, serpentinites or permanent inorganic alkaline waste, containing CaO and MgO in the form reactive with CO_2. Among such waste are f.ex.: fly ash, which are the potential material for carbon dioxide sequestration via mineral carbonation.

In the article a review of findings on the use of fly ash for CO_2 bonding via mineral carbonation has been discussed. One of the aspects of mineral carbonation of particular interest is the influence of CO_2 insertion on the leachability of chemical contamination. In the article there have been presented the exemplary results of chemical contamination contents in the leachates from 'pure' and with inserted CO_2 ash–aqueous suspensions.

The presented findings show that the insertion of CO_2 has caused changes in chemical impurities concentrations in leachates, with concentrations being either increased or decreased, however they are not great.

Key words: CO_2, fly ash from hard coal combustion, fly ash from lignite combustion, mineral carbonation, leachability

1. Introduction

The reduction of increasing anthropogenic CO_2 emission has recently become one of the most important problems as far as the environmental protection. Professional power industry is one of the biggest sources CO_2 emission. This is where a significant amount of solid waste is produced: slags, fly ash, fly ash with desulphurization products and gypsum mixtures. Fly ash is the potential material that can be used for CO_2 bonding. Polish professional power industry, which is the greatest emissioner of CO_2 in Poland, uses, above all, fossil fuel – hard coal and lignite. In 2006 CO_2 emission from Polish professional power industry amounted to 150,918 th. tons, including 91,544 th. tons from the power plants using hard coal, and 56,959 th. tons from power plants and combined heat and power plants (CHPs). At the same time 13,341 th. tons were captured, including 7,156 th. tons from power plants and CHPs operating on hard coal, while from power plants on lignite – 6,157 th. tons (Emitor 2007).

The issue of CO_2 emission reduction from power plants and CHPs may be combined with the use of fly ash for its sequestration via mineral carbonation (Uliasz-Bocheńczyk et al. 2006, Uliasz-Bocheńczyk& Mokrzycki, 2006), which is based on CO_2 reaction with metallic oxides, resulting in the formation of insoluble carbonates (IPCC…2005).

For CO_2 sequestration via mineral carbonation there may be used fly ash from fossil fuel combustion in power industry (Mazurkiewicz et al. 2004; Soong et al. 2006; Baciocchi et al. 2006; Back et al. 2006; Uliasz-Bocheńczyk & Mokrzycki, 2006), as well as ash from waste combustion (Meima et al. 2002; Costa et al. 2007).

The CaO and MgO contents determine fly ash ability to CO_2 bonding (Johnson, 2000; Back et al. 2006; Baciocchi et al. 2006). However, the reactivity of fly ash depends mainly on the CaO content, with MgO content being less important.

Mineral carbonation, or more precisely, the so called accelerated carbonation, has been suggested not only as a method of CO_2 sequestration that is emission reduction, but also as a method of chemical stabilization of fly ash not being widely used in economy, assigned mostly for deposition. This involves, first of all, fly ash from waste combustion (Costa et al. 2007, Meima et al. 2002, Zhang et al. 2007, Li et al. 2006).

In both cases, that is CO_2 sequestration and stabilization, the important issue of CO_2 usage is its impact on the impurities leachability and the change of for example pH.

2. Mineral carbonation of example ash aqueous suspensions with compositions based on fly ash from hard coal and lignite combustion

Polish professional power industry is based on the use of two main fuels for its energy production: hard coal and lignite. Fly ash from professional power industry from hard coal and lignite combustion has been used in the examinations.

Fly ash from hard coal combustion in power plant Jaworzno with CaO content – 4,94%, MgO – 2,55 and fly ash from lignite combustion in power plant Bełchatów with CaO content – 21,6%, MgO – 0,78% and free CaO – 1,1% has been used in the research. The free CaO content has not been stated in ash from hard coal combustion (Uliasz-Bocheńczyk et al. 2007).

Above all, the contents of CaO and MgO in fly ash determine the process of mineral carbonation. While comparing the contents of CaO, MgO and free CaO in the examined ash, a high CaO content (21,6%) is noticeable, in the fly ash from lignite combustion and relatively low CaO content in ash from hard coal combustion (4,94%), with no free CaO content stated in its composition.

For the purpose of confirmation of mineral carbonation processes in ash aqueous suspensions, an examination of CO_2 absorption for fresh ash aqueous suspensions as well as phase composition by means of roentgenographic method has been carried out and a supplementary study of the microstructure with the use of scanning microscope for hardened ash aqueous suspensions.

The studies of CO_2 absorption extent by ash aqueous suspensions have been carried out using especially created installation consisting of two measurement sites, including measurement sets for pressure chambers and registering devices as well as gas cylinder and reducer (Uliasz-Bocheńczyk et al. 2007).

The maximum absorption of ash aqueous suspensions on the basis of fly ash from hard coal combustion in power plant Jaworzno, has been confirmed with the ratio of ash to water 1,5 amounting to 1,22 g CO_2/100 g, for the suspensions prepared on the basis of fly ash from lignite combustion in power plant Bełchatów, the maximum absorption has been stated with the ratio of ash to water 1,25 amounting to 4,15 g CO_2/100 g (Uliasz-Bocheńczyk et al. 2007).

In the roentgenographic and microstructure studies the presence of calcite has been of particular interest, as the basic product of mineral carbonation. The presence of calcite has been stated in ash aqueous suspensions prepared on the basis of ash from hard coal combustion as well as in ash aqueous suspensions prepared on the basis of ash from lignite combustion (Uliasz-Bocheńczyk et al. 2007).

The following phases have been found in the ash aqueous suspensions with compositions based on ash from hard coal combustion in power plant Jaworzno: mullite ($Al_{4.59}\,Si_{1.41}\,O_{9.7}$), haematite ($Fe_2O_3$), quartz ($SiO_2$), calcite ($CaCO_3$) and maghemite ($Fe_2O_3$).

The following phases have been confirmed in the ash aqueous suspensions with compositions based on ash from lignite combustion in power plant Bełchatów: haematite (Fe_2O_3), quartz (SiO_2), calcite ($CaCO_3$), ettringite ($Ca_6(Al(OH)_6)_2(SO_4)_3(H_2O)_{25.7}$), calcium sulphate ($CaSO_4$), calcium silicate ($Ca_2SiO_4$), which has been confirmed by the results of examinations with the use of scanning microscope (example – Fig. 1).

In the roentgenographic examinations the presence of CSH phase has not been stated, however, it has been found in the SEM examinations in the form of gel (Uliasz-Bocheńczyk et al. 2007).

3. Leachability of chemical impurities

The leachability of chemical impurities has been carried out for ash aqueous suspensions with and without inserted CO_2 in order to determine its possible influence.

Chemical oxygen demand (COD) in the analyzed solutions of aqueous extracts has been examined according to standard PN-74 C-04578/03. The chlorides content has been marked with Volhard method, and the designation of sulphates has been done with the use of inductively coupled plasma atomic emission spectrometry method (ICP AES). The plasma emission spectrometry method has been used to mark: arsenic concentration, chrome, cadmium, copper, lead, nickel, zinc, arsenic and mercury. The findings of chemical impurities concentrations as well as the results of pH values designations and COD marking in the leachates from ash aqueous suspensions, 'pure' (without CO_2) and with the inserted CO_2 have been presented in table 1.

The insertion of CO_2 to ash aqueous suspensions prepared on the basis of fly ash from hard coal combustion as well as those from lignite combustion has caused either an increase or a decrease in concentration of various impurities in the leachates.

The insertion of CO_2 to suspensions based on ash from hard coal has brought about a decrease in the contents of Zn, Cu, As, Hg, Cd, Cr, chlorides and sulphates, and at the same time an increase in the contents of : Pb, Ni and pH.

The insertion of CO_2 to suspensions based on ash from lignite has caused a decrease in the contents of Zn, Cr, Ni as well as sulphates and chlorides, with an increase in the contents of: Cu, Pb, As, Hg, Cd and pH.

The findings have been compared with the values of the highest acceptable values of pollution indexes for treated industrial sewage stated in the Regulation of Minister of Environment on 29th November 2002 (Regulation…2002a) on conditions to fulfill while entry to water or ground of sewage as well as on the substances harmful to water environment (Journal of Laws 02.212.1799 on 16th December 2002) – annex 3, the values of acceptable leachability stated in standard – PN-G-11011 'Materials for solidifying stowage and grouting of workings', as the fly ash is, above all, economically used in mining, as well as with the requirements for water quality categories stated in the Regulation of Minister of Environment on 27th November 2002 on conditions to fulfill while using surface water deposits as drinking water (Journal of Laws 02.204.1728 on 9th December 2002).

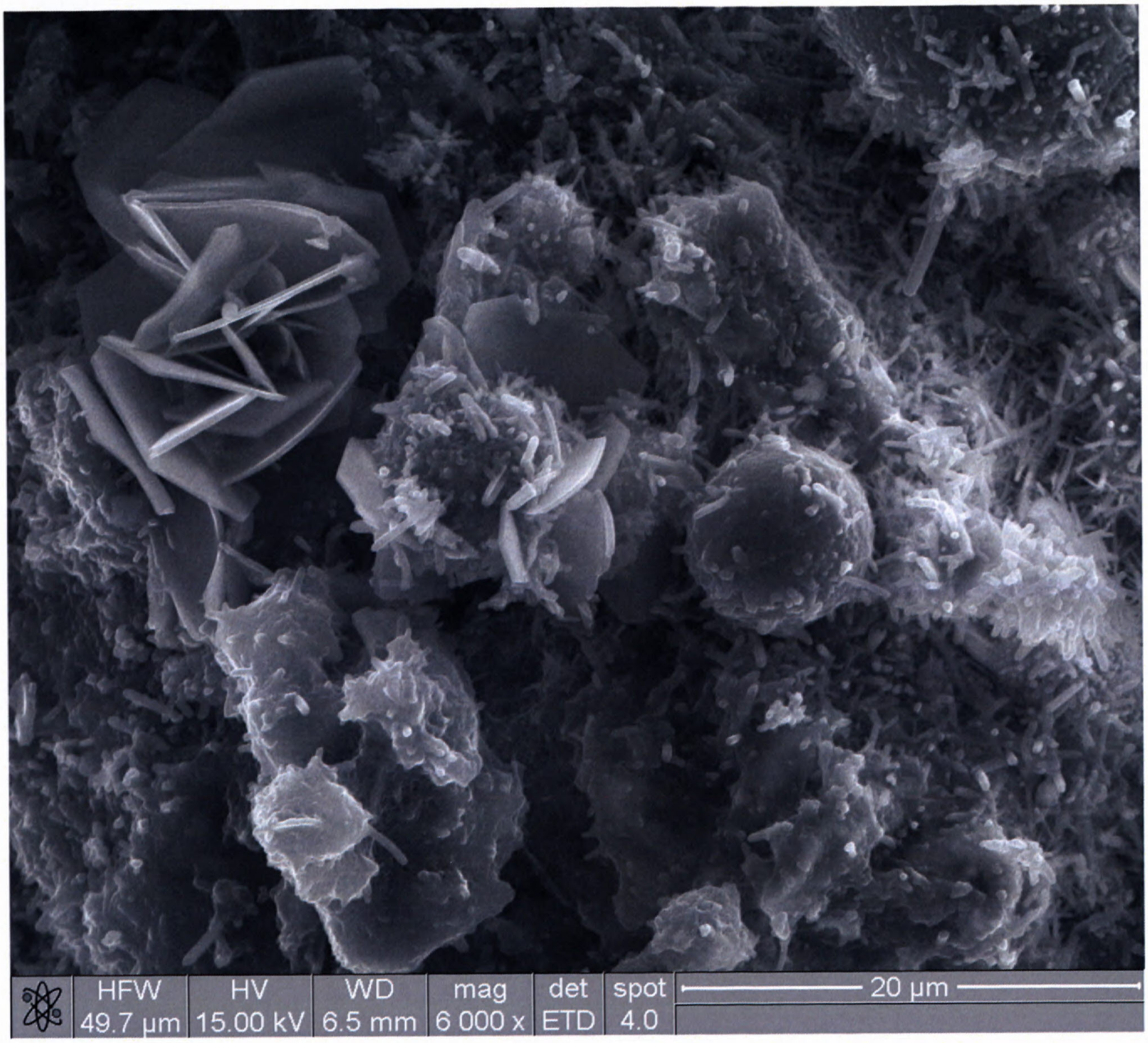

Fig. 1 Ash aqueous suspension prepared on the basis of fly ash from hard coal combustion with inserted CO_2

Table 1 Chemical impurities contents in leachates from ash aqueous suspensions 'pure' and with the inserted CO_2, mg/dm^3

Chemical impurity type	Suspension on the basis of fly ash from hard coal combustion without CO_2	Suspension on the basis of fly ash from hard coal combustion with inserted CO_2	Suspension on the basis of fly ash from lignite combustion without CO_2	Suspension on the basis of fly ash from lignite combustion with inserted CO_2
Zn	0,031	0,021	0,0080	0,0056
Cu	0,00058	0,00029	0,00037	0,00041
Pb	0,00002	0,00003	0,00003	0,00004
Ni	0,00040	0,00041	0,00024	0,00013
As	0,0118	0,0068	0,00022	0,00034
Hg	0,0044	0,0029	0,00017	0,00020
Cd	0,0011	0,00042	0,00011	0,00017
Cr	0,039	0,016	0,0065	0,006
Cl^-	7,1	3,5	1,8	0,0
SO_4^{2-}	455,9	285,7	132,8	92,0
ChZT mg O_2/L	<5,0	<5,0	<5,0	<5,0
pH	10,2	10,8	8,1	11,2

The findings have exceeded highest acceptable values of impurities indexes stated in Regulation (Regulation…2002a) for pH (acceptable 8,5 has not been exceeded only in the case of suspension with composition based on fly ash from lignite combustion without CO_2). The remaining obtained impurities concentrations were below acceptable standards.

The obtained results of chemical impurities concentrations do not exceed the values of chemical contents stated in standard PN-G-11011.

The findings of leachability have been compared with the requirements for water quality categories stated in the Regulation of Ministry of Environment on 27th November 2002 (Regulation...2002b). The obtained concentrations have exceeded the acceptable values only in the case of suspensions based on fly ash from hard coal combustion, in the case of mercury (acceptable 0,005 mg/dm^3) and sulphates (acceptable 250 mg/dm^3) and pH in the case of the two types of suspensions (acceptable 8,5 has not been exceeded only in the case of suspension with composition based on fly ash from lignite combustion without CO_2).

4. Summary

Fly ash may be the material used for CO_2 sequestration. Regardless of a low extent of absorption, as for example in suspensions based on fly ash from hard coal combustion, waste is worth considering for CO_2 sequestration, because of its great amounts. However, when deciding about ash usage for CO_2 sequestration, the leachability of chemical impurities should be taken into consideration, as far as their later use. The presented findings show that the insertion of CO_2 has caused changes in chemical impurities concentrations in leachates, with concentrations being either increased or decreased, however they are not great.

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Preliminary results of the microbiological research on CO_2 naturale exhalations executed for geobiomonitoring needs

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Abstract. Carbon dioxide storage issues require precautions and monitoring measures (geophysical, geochemical and others) being undertaken due to inspect tightness of underground sinks. Detection of possible seepage might be gained by screening local microflora that occur in soil, making use of the fact that some microorganisms proliferate the better the more carbon dioxide is supplied. The Authors decided to identify and examine those microorganisms that could be suitable to attain the aim.

Microbiological examination was performed for soil samples originating from terrains of natural CO_2 outflows (Krynica environs, S Poland). Species composition and numerosity of dominating microorganisms (bacteria, *Actinomycetes* and fungi) was defined, and one intense biochemical process was remarked. Presence of microbial physiological groups typical for highlands was detected. The results display that *Clostridium kluyverii* and nitrification process might be useful as bioindicators to estimate CO_2 supply in soil environments.

It is advisable to search for other microorganisms that might be useful and easy to apply as indicators of increased CO_2 supply in soil environment. Growth curves for *Clostridium kluyverii* and sulphur bacteria should be defined within varying CO_2 supply rates. The results obtained so far are promising, further research should be directed to other microorganisms that display desirable features to substrates other than carbon dioxide.

Key words: monitoring, storage, carbon dioxide, microorganism, bioindicator

Introduction

An underground storage of the anthropogenetic CO_2 within deep geological structures requires to monitor its plum movement within and outside of the underground sink. The gas seepage may occur through injection or observation well leaks, or through natural migration paths as faults and fractures (Moberg et al., 2002; Emberley et al., 2002). The CO_2 injection and storage monitoring may be performed using many methods, like geophysical, geochemical or other ones. They are ment to collect data on as many as possible dynamic processes referred to carbon dioxide injection into the underground sink. An importance of the carbon dioxide storage monitoring issues is considered within the 6th EU Frame Programme (e.g. CO2SINK, CO2ReMoVe), where the MEERI PAS Institute is a Partner.

The CO_2 seepage might be monitored by investigation of the local microflora composition, which is suggested by authors. It is based on the fact that some microorganisms proliferate better at higher CO_2 availability, being able to its assimilation, so the CO_2 availability increase results in their population increase (McPherson and EarthLab Steering Committee 2003). Such biomonitoring (a geobiomonitoring when referred to CO_2 exhaling from deep rock formations) is based on an assumption that CO_2 migration from the underground sink to the surface ground strata and soil shall induce detectable alteration of the local microflora. Comparing the numerosity of populations of certain microorganisms, which appear to be good CO_2 augmentation indicators, before, during and after CO_2 injection, when storage site is closed, should allow to detect possible CO_2 seepage from the underground sink (Gołębiowska & Pędziwilk, 1984; Tarkowsk & Królik 2005, Tarkowski et al., 2005, Uliasz-Misiak et al., 2006).

The literature reveals no information about existing solutions on microbiological monitoring methods used at CO_2 underground storage sites. No suitable microorganisms have been identified so far. That is why authors decided to execute microbiological research due to define: numerosity of important microbial physiological groups occurring in soil environments at higher CO_2 concentrations, such environment microbiocenotic composition and identification of indicative microorganisms sensitive to CO_2 supply. To attain the aim samples had been taken from the Złockie and Muszyna area (the region of Krynica), where occur natural carbon dioxide exhalations and its concentration in the soil air locally exceeds 10 %.

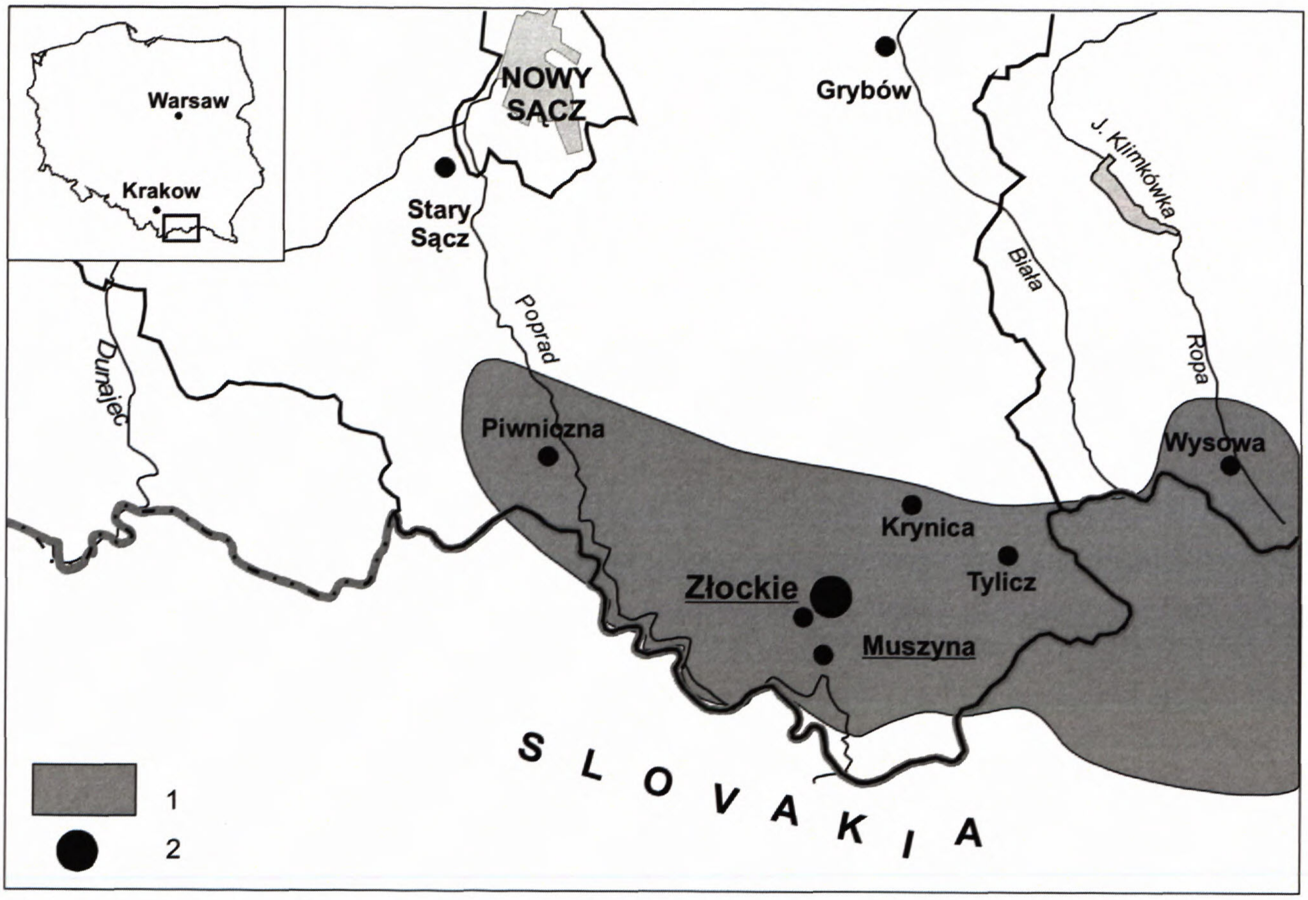

Fig. 1 Carbon dioxide exhalation occurrence within the Muszyna area (after Rajchel et al., 1999 with changes): 1- area of exhalations CO_2; 2 - the mofette at Złockie

It is thought that in a soil environment may occur 12000 – 18000 or even more different bacteria species (Barabasz & Vořišek, 2002). Calculations of certain authors show that within the whole biosphere might exist 40 000 or even 2 – 3 millions of different bacteria (Trevors & van Elsas, 1995; Tunlid & White, 1991). So it is allowed to presume that within such rich microbial diversity do exist such microorganisms that are adapted to particular conditions occurring in subject ecological microniches. It seems that CO_2 as a gas that had been present in soil environment since ever, induced microbial adaptation in a way that amongst them surely exist such ones that had adapted to its high concentrations or even require it to grow and proliferate. Such assumption was a base of the research which results are presented in the paper.

Carbon dioxide exhalations at the Carpathians (Fig. 1) are pretty widespread in the SE Poland (the Krynica environs). Their existence is combined with an endogenic carbon dioxide influx, and with tectonic zones (deep-seated faults). At surface CO_2 occurs along fractures and faults. It migrating through rocks and partially dissolves in underground water, partially penetrates into soil air forming CO_2 occurrence anomalies. The obtained soil gas composition compilation of the Krynica environs revealed an increased background at drainage area of Krynica, Muszyna and Żegiestów. CO_2 concentration average amounts 2.5 %, reaching at most several dozen percent (e.g. Złockie – 92 % of volume) (Ciężkowski et al., 2002; Leśniak, 1983). The strongest CO_2 exhalation area consists of a meadow belt between Jastrzębik and Złockie. There were found about 40 exhalation points, the biggest one is the Świdziński Mofette (Rajchel L. & Rachel J., 2006).

1. Material and Methods

Sample collection for microbiological examination to select characteristic microbes occurring in particular soil environments enriched in CO_2, and quest for indicative microorganisms sensible to alteration of soil atmosphere, were run in 2004 and 2005. The soil samples (Tab. 1) collected for detailed microbiological analyses originated from Muszyna/Krynica region, where CO_2 concentration in soil air from several to 20 and more percent. The soil samples weighted from 500 g to 1000 g, were taken from 2 depths: 1st level 0 – 15 cm and 2nd one at 40 - 50 cm, to sterile plastic containers, respecting all the microbiological cleanness rules. For complete characteristics of the investigated soils their humidity and pH reaction were defined. The probes were taken from Złockie location (probes 1 and 2) and from Muszyna location (probes 3 and 4), from the two mentioned depths. Totally there were collected 8 soil samples out of 4 locations. The sample No 1 was taken from a meadow by the „Devil's Breath" spring (soil rich in humus). The sample No 2 was

Table 1 Location of sampling points

Point	Localisation	Latitude	Longitude	Altitude [m a.s.l.]	CO_2 concetration
1	Złockie – the meadow by the „Devil`s Breath" spring	49°23'12.1"	20°53'51.7"	572	>25%
2	Złockie – the escarpment by the road, to the north, below the shrine (loam)	49°23'20.6"	20°54'25.9"	575	4%
3	Muszyna – the meadow by minera water well P-3	49°20'48.3"	20°53'03.8"	422	8.6%
4	Muszyna by mineral water well P-3	49°20'48.0"	20°52'56.8"	438	>25%

Table 2 Media used for microbiological tests (microorganism isolation and definition)

No	Microbiological media	Defined microorganisms and physiological groups
1	Agar MPA	General bacteria number - vegetative forms
2	Agar MPA	General bacteria number - resting forms
3	Pochon's agar	General number of Actinomycetales
4	Pochon's agar	General number of thermophile Actinomycetales
5	Ammonificator agar	Bacteria active in organic nitrogen metabolism
6	Pikowska – medium	Bacteria active in phosphorus metabolism
7	Ashby – medium	Bacteria combining N_2 from air - *Azotobacter*
8	Mash- agar	General number of fungi
9	Pseudomonas medium	*Pseudomonas saccharophila*
10	Desulfovibrio - medium	*Desulfovibrio* in CO_2 atmosphere
11	Desulfovibrio - medium	*Desulfovibrio*
12	Clostridium - agar	*Clostridium pasteurianum* denomination
13	Starch medium	Bacteria active in starch decay, amylolytic bacteria
14	Winogradsky – medium	Nitrification process activity
15	Winogradsky – medium	Nitrification process activity in CO_2 atmosphere
16	Giltay – medium	Denitrification process activity
17	Cl. kluyveri – medium (liquid and solid)	**Clostridium kluyveri**
18	Cl. kluyveri – medium (liquid and solid)	*Clostridium kluyveri* in CO_2 atmosphere

taken from a slope by the road, to the north, below the shrine (loam). Samples No 3 and No 4 were taken in Muszyna, by mineral water capture well P-3, from a meadow above the well and from nearby the well respectively.

The laboratory examinations had let to define quantity and species composition of dominating microorganisms existing in the examined soils. To microbiologically characterize the examined soils standard methods of microbiological analysis were used, as well as specific and selective media shown in the table 2. For qualitative examinations of systematic of dominating bacteria and fungi species the standard methods of analysis were used, commonly applied in microbiological laboratories, based on recognized tests and manuals: Bergey`s for bacteria and Domsch`s for fungi.

For a quest for indicative microorganisms able to better, faster or particular growth culture methods that involve special chambers equipped with atmosphere composition control were used. First of all a growth of specific anaerobic bacteria like *Clostridium kluyveri, Pseudomonas saccharophila and Desulfovibrio* (Jungermann et al., 1968) were remarked. The cultures were kept in an anaerostatic chamber in controlled atmosphere. As the next step a response of nitrifying bacteria to higher CO_2 concentration was observed.

2. The results

The qualitative and quantitative results were obtained due to performed detailed microbiological research and they are shown. Numerosity of the selected microbial groups is shown in the table 3. Numerosity of the selected microbial groups displayed in (log – E) system, for each sample, is shown by the figures 2 and 3.

The quantitative results (Tab. 3) and charts (Fig. 2 and Fig. 3) that concern different microbial group occurrence reveal that their amount alters strongly depending on the sample collection location. This diversity is interfered with humidity, reaction and CO_2 concentration. Large diversity of fungi, thermophyllic *Actinomycetes* and denitrifying bacteria was observed in individual samples. It is probable that amongst these groups occur the microorganisms quested for, that might indicate higher CO_2 concentration in a soil environment. To prove these presumptions further, detailed and expert investigation is required. The most numerous bacterial physiological groups present in examined soils are: active bacterial forms, read on MPA agar media, and ammonifying bacteria, active in organic nitrogen cycle. Moreover, amongst the most numerous microorganisms defined occur bacteria selected to display CO_2 supply changes, that means *Pseudomonas saccharophila* and *Clostridium kluyverii.*

Table 3 Numerosity estimation of microorganisms present in chosen soil profiles taken out from Muszyna environs

Microorganisms and physiological groups	Samples							
	1-1	1-2	2-1	2-2	3-1	3-2	4-1	4-2
Bacteria - vegetative forms	60060000	1869250	20367750	11035500	21879500	23572000	8959000	4165500
Bacteria - resting forms	32564000	2145870	15650750	2568750	14698000	19124500	4895200	1700500
Actinomycetales	1633	0	467	267	46200	18133	18500	19867
Thermophile Actinomycetales	0	0	0	0	5833	833	0	3333
Ammonificator	12162500	23691250	2988750	7250	19242000	5745500	1493500	55750
Phosphorus bacteria	290	13	0	1500	0	73	5033	1747
Azotobacter	833	37	0	0	4667	10333	2667	333
Fungi	1767	6800	11433	1000	20433	27200	16133	23833
Pseudomonas saccharophila	2110904	10440	101140	151424	1590116	748114	960088	438184
Desulfovibrio in CO_2	8160	2700	35	500	7000	8000	220	3310
Desulfovibrio sp.	1406000	13333	526000	270000	369333	486667	690000	424000
Clostridium pasteurianum	1.E+02	1.E+03	1.E+02	1.E+03	1.E+03	1.E+02	1.E+01	1.E+03
Amylolytic bacteria	1.E+05	1.E+04	1.E+03	1.E+03	1.E+05	1.E+06	1.E+05	1.E+04
Nitrifying bacteria	1.E+09	1.E+09	1.E+07	1.E+09	1.E+05	1.E+09	1.E+07	1.E+09
Nitrification in CO_2	1.E+08	1.E+10	1.E+09	1.E+09	1.E+06	1.E+10	1.E+08	1.E+10
Denitrification	1.E+06	1.E+03	1.E+03	1.E+04	1.E+07	1.E+07	1.E+06	1.E+06
Clostridium kluyveri	1.E+05	1.E+03	1.E+02	1.E+02	1.E+06	1.E+04	1.E+03	1.E+04
Clostridium kluyveri in CO_2	1.E+06	1.E+04	1.E+04	1.E+04	1.E+06	1.E+04	1.E+05	1.E+04
pH	6.45	6.55	4.79	6.10	5.9	6.14	6.48	6.20
Humidity [%]	49.20	33.10	16.40	13.90	15.50	17.40	10.10	8.70

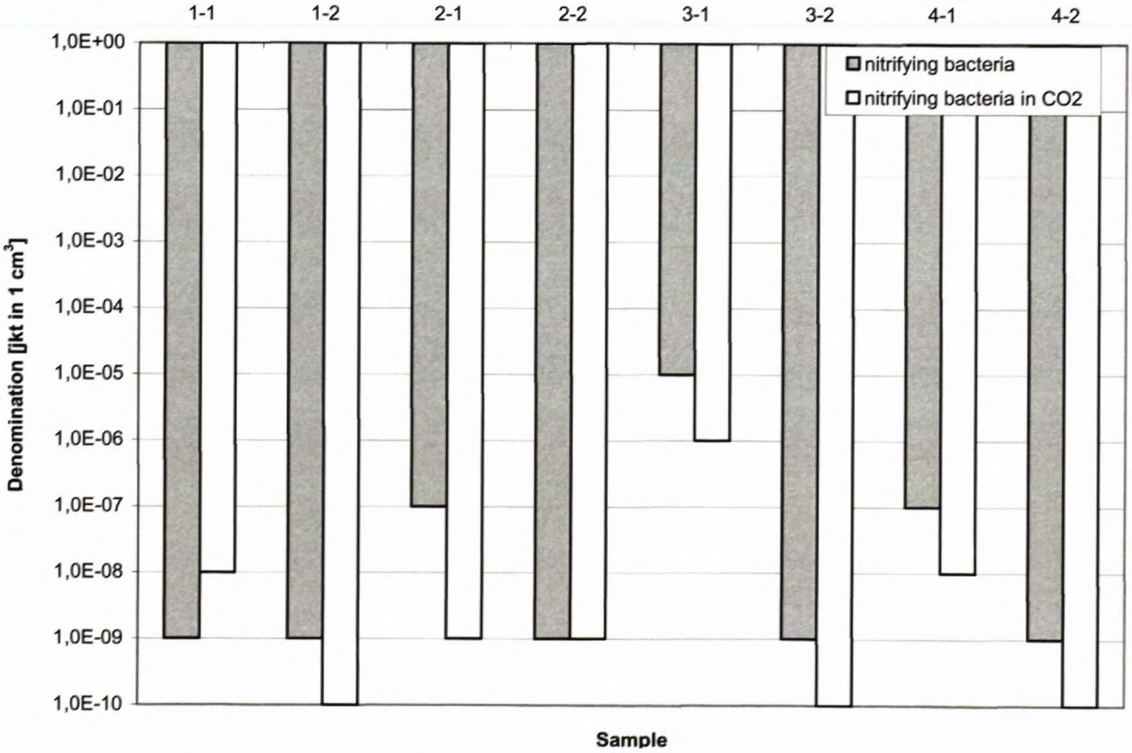

Fig. 2 Denomination of nitrifying bacteria present in examined soils, cultured in higher CO_2 concentration

Results reveal that a nitrification process occurs in the examined soils very intensely, which may suggest that increased CO_2 supply in soil environment increase the process.

On the other hand qualitative examinations (Tab. 3) of microbiocenotic composition of occurring bacterial species, Actinomycetes and fungi tell that the examined samples reveal typical soil microflora characteristic for highlands rich in organic matter. The examined nitrification process, though of oxygenic nature, displayed response to increased CO_2 concentration, and its intensity was exceptional. Denomination of nitrifying bacteria pre-

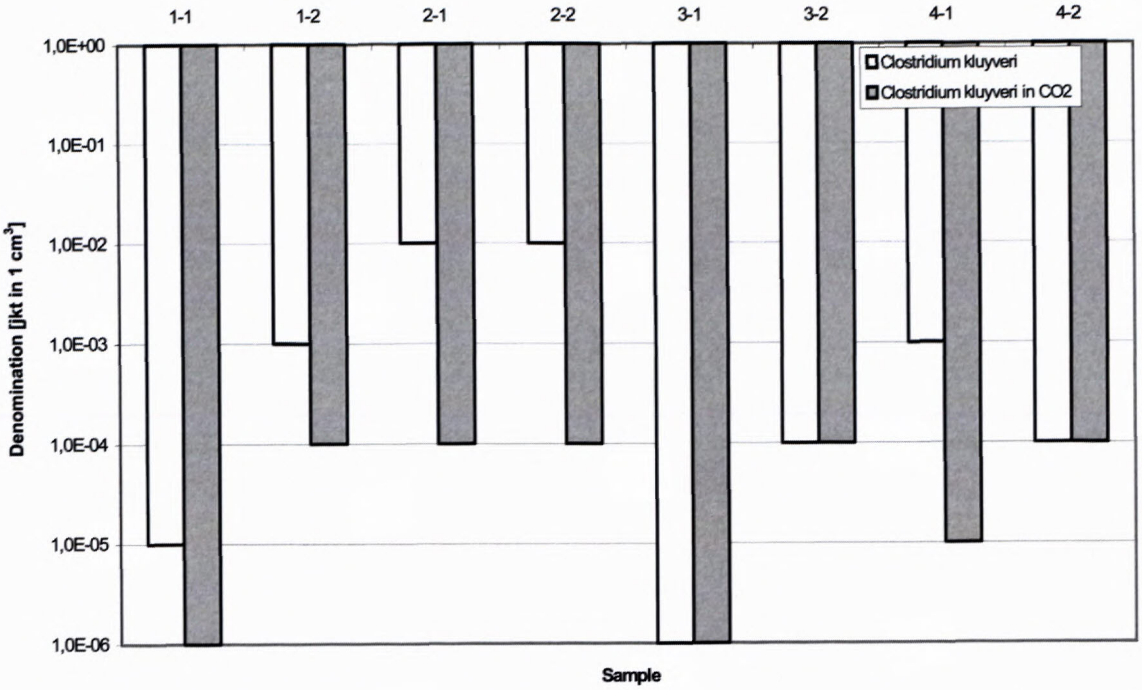

Fig. 3 Denomination of Clostridium kluyveri bacteria present in examined soils, cultured in higher CO_2 concentration

sent in some samples (No 1-1, 1-2, 3-2, 4-2) (Fig. 1) was very high (10^{-9}) which is pretty rare in cultivated soil, even in lowlands. Observations of the *Clostridium kluyveri* bacteria, which revealed the most significant diversity, reaching 4 magnitude orders (balancing between 10^{-2} and 10^{-6}) in the examined soil samples revealed that it is the most suitable microorganism fit to choose and define locations of high CO_2 concentration.

Results of research run in higher CO_2 concentration allow to state that population of nitrifying bacteria and *Clostridium kluyveri* ones do response readably to CO_2 concentration increase, in laboratory conditions. The numerosity increase (Fig. 2 and 3) is perceptible in most of locations and reaches multiplication index from 10 to 100 times, referring to initial number. It seems to be independent from the sample collection depth, for both cases. However it could depend on initial microorganism numerosity.

3. Discussion

The performed detailed microbiological examinations of soil probes collected from two depths revealed that there occur all investigated microbial physiological groups, which shows high biological activity of these soils. A special interest should be paid to extremely high number of ammonifying and nitrifying bacteria, as well as *Azotobacter* gender ones, which could be combined with high fertility of these lands. The bacteria of special interest, that is *Clostridium kluyveri* and *Desulfovibrio sp.* occurred in all examined samples. Relatively high number of typically anaerobic bacteria could suggest their accommodation to conditions existing in soils of higher CO_2 concentration.

The quantitative research reveals that Muszyna region soils are rich in different microorganisms. Bacteria, their vegetative forms as well as resting forms, are present in population of several millions to several dozens of millions of cells in one gram of soil. There occur as well bacteria active in nitrogen, phosphorus and sulphur cycles, in large quantities. A special attention should be paid to *Azotobacter* sp. bacteria, that occur in these soils in extremely large quantities. As far as this bacteria is considered it is usual for fertile soils, rich in mineral compounds and organic substance. The isolated microorganisms, bacteria, *Actinomycetes* and fungi, are typical for highland brown soils, rich in organic matter. Existence of different microbial groups at extremely high concentrations and very intensive processes running in these soils could suggest that higher CO_2 supply intensify growth, proliferation and biochemical processes of the selected microbial groups.

Basing on initial numerosity of the indicative soil microflora one cannot deduce the CO_2 concentration in soil air. Only observation of the numerosity variation in time allows such deduction. To consider just variation induced by CO_2 supply it is required to define CO_2 concentration alteration caused by other environmental factors (periodical changements). It requires an initial period of observation of the future sequestration site area, or else adaptation or reinterpretation of already existing results of observation of another, similar area.

Amongst aerobic microorganisms, as well as among anaerobic ones, there may exist species or strains that response to increased CO_2 concentration in soil air, by increased growth or by increasing intensity of particular biochemical processes. Isolation of other but similar microorganisms, would allow using them as next bioindicators or biosensors sensible to increased CO_2 contents in soil air.

A well-defined diversity CO_2 occurrence in soil air at the same area, dependent on location of sampling point and measuring point suggests to set a relatively dense and detailed sampling grid on terrains to be geobiomonitored in the future.

Basing on the results obtained so far from already performed microbiological tests and observation of soil environment at chosen locations by Krynica it is possible to present following general conclusions:

1. As a result of detailed microbiological analysis of examined soil environments it was displayed that there occur all examined microbial physiological groups, which diversity came out of local habitat conditions.

2. Observed carbon dioxide concentrations in soil air at the area of natural CO_2 exhalations differ each other significantly, depending on location of the exploration point.

3. Obtained results reveal that *Clostridium kluyveri* bacteria and the nitrification process can be used as indicators to estimate CO_2 contents in soil environments.

4. Initial number of indicative microorganisms does not reflect directly CO_2 concentration in soil air.

5. It is advisable to search for other microorganisms (e.g. fungi, thermopile *Actinomycetes* or denitrifying bacteria) that might be suitable for and easily applicable as indicator of increased CO_2 contents in soil environments.

6. Further quest for indicative microorganisms reflecting CO_2 high concentrations in soil environment should be run in field and laboratory conditions as well.

Obtained preliminary results allow to run further microbiological and biochemical research, focused on detailed definition of growth curves for found Thiobacillus thiooxidanssulphur bacteria and *Clostridium kluyveri*, within a range of CO_2 concentrations, and focused on elaboration of methodology allowing to count bacterial cells present on surface of a poor medium (e.g. pyrite).

Concurrent existence of two physiological groups sensitive to CO_2 supply in soil microflora increase credibility of the results obtained so far. Increase of bioindicators number analyzed in geobiomonitoring process reduce its susceptibility to clutter. Regarding these reasons it is advisable to run further research on bioindicator quest, widening spectrum of interest to substrates other than CO_2.

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CO_2 emissions and geological storage possibilities in the Czech Republic

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Abstract. A study focused on CO_2 capture and storage potential of the Czech Republic was performed within the CASTOR and EU GeoCapacity European R&D projects. The first part of the study focuses on country-wide greenhouse gases emissions, their development and related national policies. A comprehensive inventory of big industrial CO_2 emission point sources follows based on both data from the National Allocation Plan and monitoring and reporting results for the EU Emission Trading Scheme. The second part deals with the national geological settings of the Czech Republic. Big sedimentary basins were evaluated regarding their suitability and potential for geological storage of CO_2 and several tens of promising structures were selected, representing all the three main types of storage structures – deep saline aquifers, hydrocarbon fields and unmined coal seams. The first rough assessment of storage capacities of the selected structures was made, resulting into a total figure of ca 3300 Mt CO_2, which can be regarded the first estimation of the country-wide CO_2 storage potential. Deep saline aquifers, representing almost 87 % of this capacity, are the most important structures from the quantitative point of view.

Key words: Greenhouse gases, carbon dioxide, CO_2 capture and storage, , ,CO_2 emissions, CO_2 storage capacity.

1. Introduction

The Czech Republic counts among countries with high level of CO_2 emissions in terms of per capita and per GDP unit values. This is the reason why various options of their reduction are placed on the agenda. Among these options, CO_2 capture and storage (CCS) seems to be one of the most effective, especially in relation to big stationary sources like power plants, refineries, steel mills or cement factories. To be able to assess the territorial CCS potential of the country, a detailed study focused on big CO_2 emission sources (exceeding 100 kt CO_2 / year) was performed, accompanied by a review of the national geology resulting into selection of geological structures potentially suitable for geological storage of CO_2.

2. Greenhouse gas emissions in the Czech Republic

Protection of the climate system of the Earth is a top-priority environmental issue in the Czech Republic (CR). It is included in the Resolution No. 187/2004 of the Government of the CR (National Program to Abate the Climate Change Impacts in the Czech Republic) and also in the Actualized State Environmental Policy of the CR (2004). The Czech Republic has committed itself to reduce its greenhouse gas (GHG) emissions by 8 % from the base year (the emissions in 1990 for CO_2, CH_4 and N_2O, but 1995 for F-gases) in the first commitment period (2008 – 2012) of the Kyoto Protocol. It is believed, that the CR will be able to fulfill this goal without serious problems.

Moreover, in 2001 a national target was declared by the Czech government in the State Environmental Policy to reduce GHG emissions in 2005 even by 20 % compared with the year 1990. From GHG emission data for period 1990 – 2004 it is evident that this target will be met (see Fig. 1). Much more ambitious targets are incorporated in the National Program to Abate the Climate Change Impacts in the Czech Republic - to reduce CO_2 emissions per capita by 30 % until 2020, compared to 2000; to reduce total aggregate CO_2 emissions by 25 % in 2020, compared to 2000; and to keep at the commenced trend to 2030. Considering these ambitions, it is clear that development and application of new advanced technologies (including CO_2 capture and geological storage) are highly desirable.

Greenhouse gas (GHG) emission inventories in the CR are compiled according to the standard IPCC methodology and the results are submitted annually to the United Nations Framework Convention on Climate Change Secretariat (UN FCCC) in standard formats. The Czech Hydrometeorological Institute (CHMI) is responsible for GHG inventory preparation on the territory of the CR. Result of these inventories is shown in Fig. 1. In 2006, the total aggregated emissions (including removals from the LULUCF sector) reduction was almost 23.9 % compared to 1990. It is evident that CO_2 represents a thumping majority (85.9 %) of all GHG emissions, while contributions of CH_4, N_2O and F-gases are 8.3 %, 5.1 % and 0.7 %, respectively (CHMI, 2006; CHMI, 2007, CHMI, 2008; Fott, Vácha 2005).

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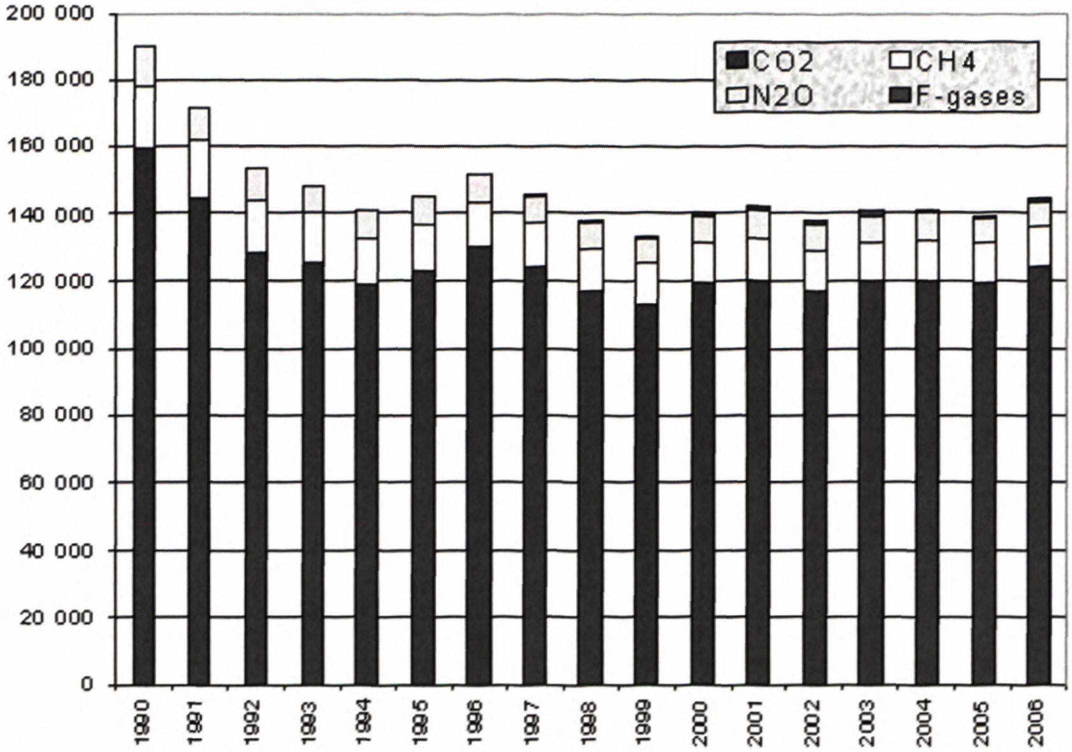

Fig. 1 Total aggregated greenhouse gases emissions in the CR in 1990 – 2006 [kilotonnes CO_2 equivalent]

Recently, a new source of data on individual CO_2 emission sources has appeared. It contains data collected for the purposes of the European Union Emissions Trading Scheme – EU ETS. All major CO_2 emitters (stationary point sources) are included in this scheme. In addition, all facilities under EU ETS are obligated to regularly monitor and report their CO_2 emissions

Since 1990, the emissions reduction in the CR was much higher than in the EU, especially due to the industry restructuring in the first period of the 1990s. On the other hand, further reduction after 1995 was supported by the implemented policies and measures (mainly oriented to energy efficiency, usage of natural gas and biomass, etc. – see below). A comparison of GHG emissions development in the EU and the CR is shown in Figure 2.

A number of measures have been implemented in the CR, leading to a decrease in GHG emissions. These include measures limited to certain specific subject or sector (e. g. the State program for energy savings and use of renewable energy sources, etc.), as well as framework measures (e.g. the National Program to Mitigate Climate Change). The majority of these measures were primarily oriented towards energy efficiency and/or air quality (clean air) and the GHG/CO_2 emissions reduction was a side effect only. The EU Emission Trading System (EU ETS), established recently, represents the fist measure oriented primarily on greenhouse gas emissions reduction. At the same time it must be stated that the emissions reduction achieved in the energy and industrial sectors are – to a significant extent - negated by the increase of CO_2 emissions generated by transport.

Notwithstanding the achieved emissions reduction since 1990, some relative indicators show high GHG emission figures for the CR, e. g. emissions per capita or per GDP unit (see Figure 3). It is mainly due to the wide use of brown coal, the relatively low energy efficiency and the relatively low GDP level. This is another reason why it is very important to reduce GHG emissions in the CR.

3. CO_2 emissions from individual facilities covered by EU ETS

For the 1st period of EU ETS (2005-2007), about 97 mill. allowances were annually allocated by NAP I (First national allocation plan) among Czech facilities (installations) which are taking part in EU ETS. In general, amount of allowances allocated per year were above the real amount of monitored, verified and reported emissions in years 2005 (82.5 mill. t.) and 2006 (83.7 mill. t.) and it will probably be the same case in 2007. For the 2nd period of EU ETS (2008-2012), about 86.8 mill. allowances will be annually allocated by NAP II (Second national allocation plan).

There are a few reasons of difference between reality and NAP I:

– The amount of allocated allowances includes also bonuses for “early actions” and other bonuses which increase the number of allowances in comparison to historical emissions;

– Real emissions are positively affected by intentional saving measures (usage of biomass, natural gas etc.) in order to sell surplus allowances;

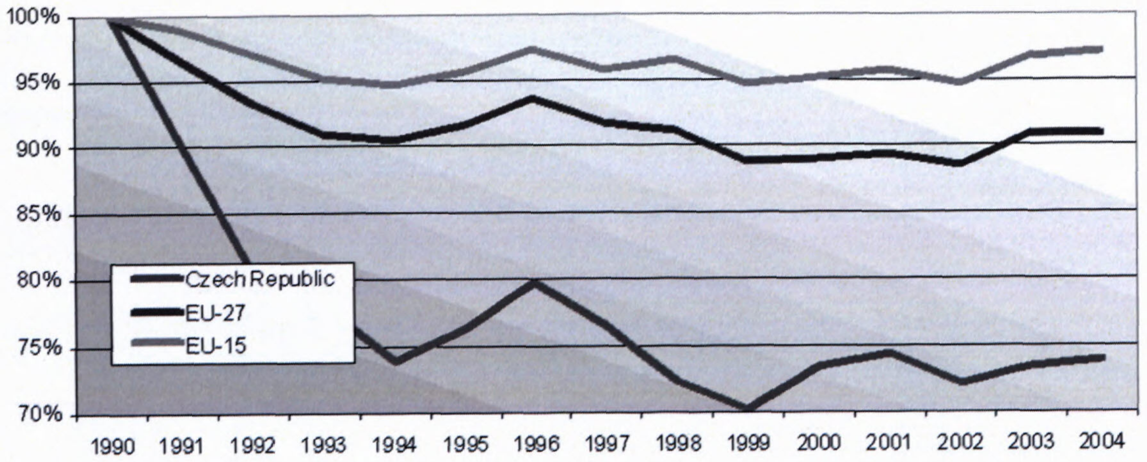

Fig. 2 Comparison of GHG emissions development in Czech Republic and in the EU

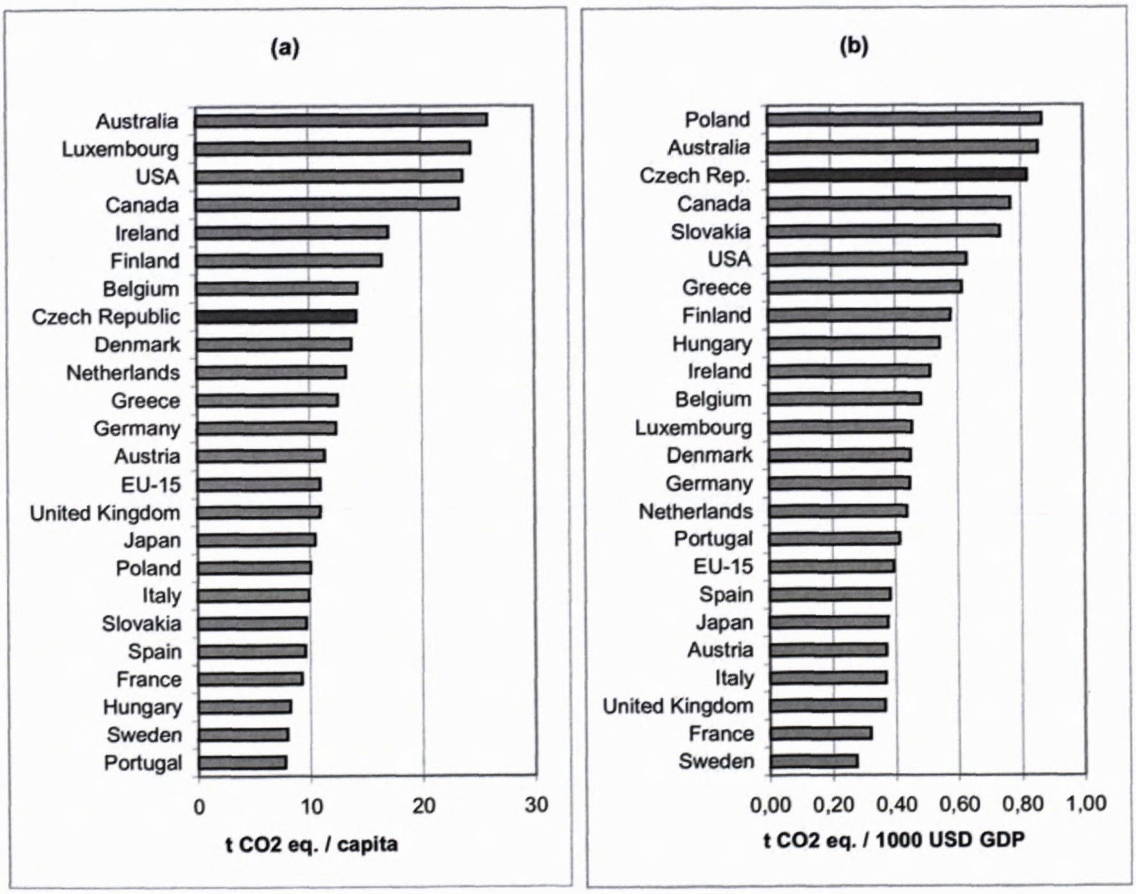

Fig. 3 Comparison of GHG emissions per capita (a) and per GDP unit /recalculated according to purchasing power parity/ (b) in 2003

Allowances are allocated for three-year period, which reflects the expectation of gradual economic growth and real emissions were monitored only for the first year of this period;

– Real emissions were probably generally underestimated and/or data used in NAP preparation were overestimated.

In the following paragraphs we use two approaches of representing CO_2 emissions from individual facilities:

I Emissions approximated by amount of allocated allowances per year by NAP for the period 2005 – 2007;

II Emissions expressed as really monitored, verified and reported in 2005.

Approach I: Emissions approximated by allocated allowances

According to the Czech national GHG inventory (CHMI, 2006), annual CO_2 emissions from the whole area of the Czech Republic were approximately 127 million in 2004. More than 76 % of it (97 mill. t) are covered by stationary industrial point sources. To obtain information about geographical distribution of CO_2 emissions, an inventory of emission point sources bigger than 100 000 t CO_2 per year has been created. These sources are responsible for 91 mill. t of annual CO_2 emissions which represents 71.7 % of total Czech CO_2 emissions and 93.8 % of emissions from stationary point sources (see Tab.1).

Tab. 1 Overview of CO_2 emissions in the Czech Republic (Approach I

Type of emissions	mill. t / yr
Total CO_2 emissions from the whole area of the Czech Republic	127
CO_2 emissions from sources covered by EU Emission Trading System (NAP)	97
CO_2 emissions from facilities emitting more than 100 kt CO_2 per year	91
CO_2 emissions from facilities emitting more than 500 kt CO_2 per year	80
CO_2 emissions from facilities emitting more than 1 Mt CO_2 per year	68

Data sources for establishing CO_2 emissions from individual stationary sources were in this case (Approach I):

- First National Allocation Plan of the Czech Republic (for the EU Emission Trading Scheme);
- National Integrated Pollution Register of the Czech Republic (under IPPC Directive).

Both data sources are open to public. The First National Allocation Plan (NAP I) has been prepared by the Ministry of Environment, in cooperation with the Ministry of Industry and Trade, based on the data obtained by the Czech Hydrometeorological Institute. The Integrated Pollution Register (IRZ) has been set up by the Ministry of Environment and is run by the Czech Environmental Information Agency (CENIA).

Emission data from the National Allocation Plan (NAP) should represent a suitable assessment of CO_2 emissions for the period of 2005 – 2007 because the allocation of emission allowances is based both on historical emission data (since 1999) and expected progress of national economy in future. According to the NAP, 87 major point sources producing more than 100 kt of CO_2 per year have been identified. 19 of them are power plants, 31 heating facilities, 12 energy producers for manufacturing industry, 8 metallurgical plants, 10 cement & lime works, 3 refineries and 4 other facilities. 22 of the above mentioned facilities emit more than 1 Mt CO_2 per year and 18 of them between 500 – 1 000 kt per year. These two groups represent almost 82 % of national CO_2 emissions from stationary industrial point sources. The share of individual industry sectors in total CO_2 emissions of the country is shown in Tab. 2.

Geographical distribution of Czech stationary industrial point sources is shown in Fig. 4. It is obvious that the sources are concentrated especially in the NW and NE part of the country.

The concentration of CO_2 in exhaust gases is usually lower than 20 % because the combustion processes are performed in the air atmosphere (21 % O_2, 79 % N_2).

Tab. 2 Share of industry sectors in total CO_2 emissions

Sector	Emissions [t/yr]	Share [%]	Number of facilities
Power	55 243 423	60,8	25
Heat	10 335 207	11,4	27
Chemicals (other)	5 373 587	5,9	7
Refineries	1 317 766	1,5	3
Iron and Steel	12 597 603	13,9	7
Paper and pulp	778 672	0,9	3
Cement	2 974 603	3,3	5
Other*	2 186 609	2,4	10
Total	**90 807 470**	**100.0**	**87**

* lime, glass, coke production, natural gas compress station

Nevertheless, two exceptions could be identified (= "good opportunities for carbon capture") where the CO_2 concentration is much higher. These sources are marked as "Early opportunities" in the map in Fig.4.

The first case is the ammonia production at Chemopetrol, a.s., Litvínov. The process includes production of hydrogen by gasification of residual fuel oil by steam oxygen mixture. Gasification is followed by the shift reaction: $CO + H_2O = CO_2 + H_2$. CO_2 is separated from H_2 by low temperature absorption (RECTISOL), H_2 is used for ammonia synthesis by reaction with N_2. The assumed amount of CO_2 produced is about 700 kt per year. This source seems to be very perspective for CO_2 a pilot capture and storage application.

The second case is the Sokolovská uhelná, a.s. plant in Vřesová, consisting of two sources: (i) classical heating plant emitting about 60 % of total CO_2 amount and (ii) steam-gas cycle power plant, emitting the remaining 40 % of CO_2, based on gasification of brown coal by steam–oxygen mixture. Even in this case about 700 kt CO_2 per year are captured by the RECTISOL process and after that released to the atmosphere.

Approach II: Real CO_2 emissions from facilities covered by EU ETS in 2005

CO_2 emissions from individual facilities (installations) covered by EU ETS are monitored and reported according to Decree of the Ministry of Environment No. 696/2004 that represents the Czech implementation of the Decision of European Commission No. 2004/156/EC which is generally called "Monitoring and Reporting Guidelines". Monitoring is based mostly on calculations from consumption of individual fuels (or material) and from relevant emissions factors (Fott et al., 2006). Before submission to the "competent authority" (Ministry of Environment) the report on monitoring has to be verified pursuant to Act No. 695/2004 Coll. that is Czech implementation of Directive 2003/87/EC generally called as "Directive on EU ETS".

Similar emission statistics as presented for Approach I are given in Tables 3 and 4.

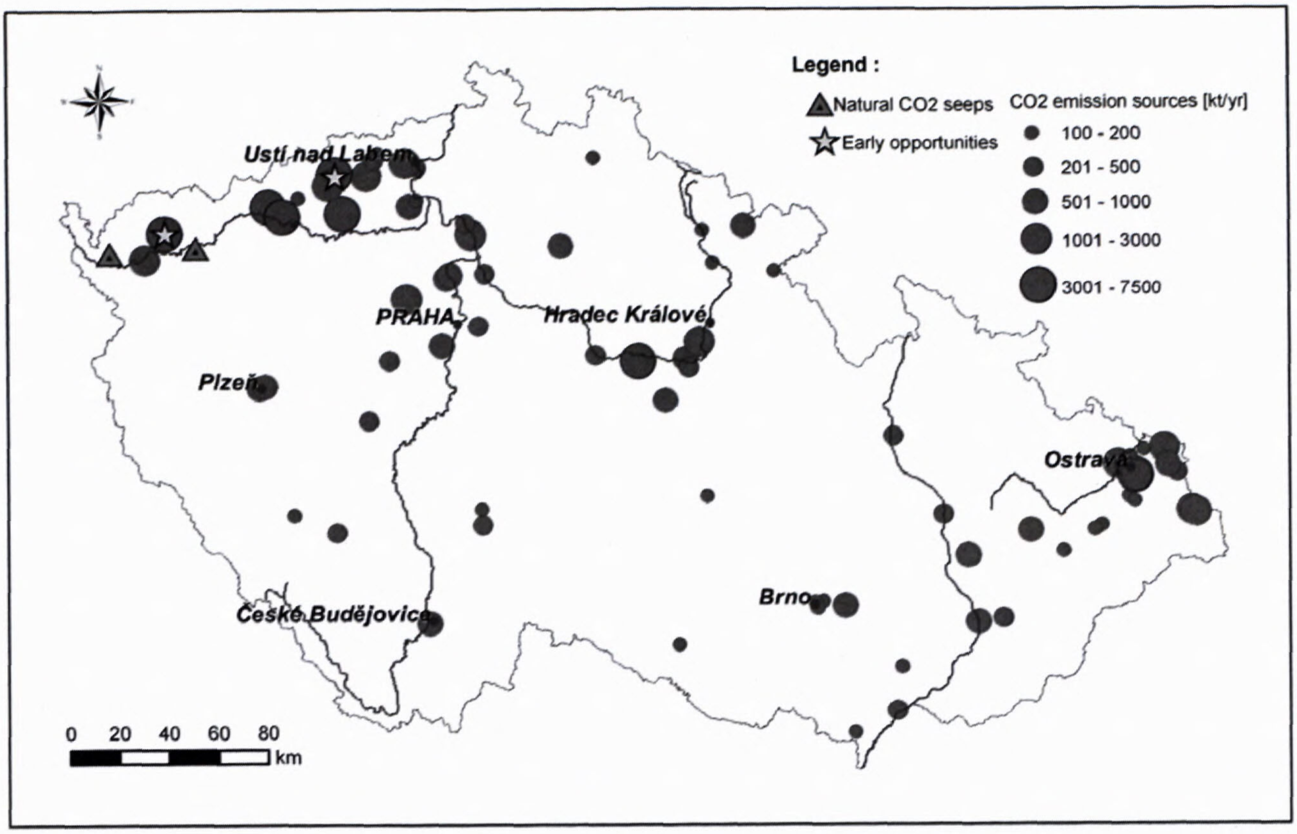

Fig. 4 Map of CO_2 emission sources in the Czech Republic (pointspurces emitting more than 100 kt CO2/year)

Tab. 3 – Overview of CO_2 emissions in the Czech Republic (Approach II)

Type of emissions	mill. t / yr
Total CO_2 emissions from the whole area of the Czech Republic, National Inventory	127
CO_2 emissions from sources covered by EU Emission Trading System (2005)	82
CO_2 emissions from facilities emitting more than 100 kt CO_2 per year	77
CO_2 emissions from facilities emitting more than 500 kt CO_2 per year	65
CO_2 emissions from facilities emitting more than 1 Mt CO_2 per year	60

Tab. 4 – Share of industrial sectors in CO_2 emissions covered by ETS (Approach II)

Sector	Emissions [t/yr]	Share [%]	Number of facilities
Power	49 145 177	63,0	25
Heat	8 849 058	11,3	27
Chemicals (other)	4 540 421	5,8	7
Refineries	969 327	1,2	3
Iron and Steel	9 866 977	12,6	7
Paper and pulp	454 158	0,6	3
Cement	2 553 038	3,3	5
Other*	1 652 271	2,1	10
Total	**78 030 427**	**100.0**	**87**

* lime, glass, coke production, natural gas compress station

4. General geology – sedimentary basins

The territory of the Czech Republic belongs to the Bohemian Massif (western part) and the Carpathians (eastern part). A significant part of the area is formed of crystalline rocks. Nevertheless, several major sedimentary formations, representing potentially suitable CO_2 storage areas, can be found (Mísař et al., 1983; Picha et al., 2006):

Tertiary:

- Vienna Basin (Czech part) is located in SE part of the Czech Republic. The age of the sediments is Miocene (from Eggenburg to Pontian). This basin is the oldest oil and gas industry area in the CR.
- Carpathian Foredeep (Czech part) is a narrow basin oriented SW – NE, limited from SE by the Carpathian Flysch Zone. The sediments are of Miocene origin (Ottnangian? - Karpathian – Badenian). Some oil & gas structures can be found here.
- Carpathian Flysch Zone is located at the Czech – Slovak border. It is composed of folded Carpathian nappes (mainly Tertiary sandstones and claystones). The basement of the napes is formed by Miocene sediments of the Carpathian Foredeep. Below them, Mesozoic and Palaeozoic sediments can be found. In some parts, however, the pre-Tertiary basement of the nappes is formed by crystalline rocks. All the autochthonous sediment formations, as well as the weathered parts of the crystalline complexes represent important oil & gas and aquifer structures.

- Sub-Krusne hory Mountains Basins comprise 3 basins - Cheb, Sokolov and North Bohemian Basin. The sediments are of Eocene, Oligocene and lower Miocene age. The basement of these basins is composed of Carboniferous and Cretaceous sediments. Active brown coal open pits are located in the Sokolov Basin and in the North Bohemian Basin. In general, the basins are too shallow and do not include structures suitable for storage of CO_2.

Tertiary and Cretaceous:

- South Bohemian Basins comprise 2 basins - Budejovice and Trebon - in the south of the CR. Their sediments are of Cretaceous and Miocene origin. Small brown coal open pits were located in the Budejovice Basin (no more active). The basins are too shallow for CO_2 storage purposes.

Cretaceous:

- Bohemian Cretaceous Basin is one of the largest basins in the CR. It is located in the middle of the Bohemian Massif. The sediments are of Cenomanian – Santonian age. This basin is an important groundwater reservoir and as such it is not suitable for CO_2 storage. The basement of the basin is partly built of Permian-Carboniferous sediments (see below) with interesting aquifer structures and coal measures.

Permian-Carboniferous:

- Lower Silesian Basin (Czech part) is located in the north of the CR. The sediments are of Lower Carboniferous (Tournaisian) – Upper Permian age. Coal mining activity was stopped here in the early 1970s. The basin contains an interesting aquifer structure for potential CO_2 storage.
- Central Bohemian Basins represent a chain of typical limnic basins, located along the line Plzeň – Prague - Mladá Boleslav. Coal mines were located mainly in the Plzeň Basin, the Rakovník Basin and the Kladno Basin. The last coal mine in this area was closed in 2003 (in the Kladno Basin). The sediments are of Upper Carboniferous (Westphalian) – Lower Permian origin. The Permian-Carboniferous sediments continue from Central Bohemia to the Lower Silesian Basin under the Cretaceous sediments of the Bohemian Cretaceous Basin. Several promising aquifers as well as coal-bearing structures are located within this stratigraphic unit.

Carboniferous:

- Upper Silesian Basin (Czech part) is located in the NE of the CR. Its sediments originate from Tournaisian – Westphalian. There are two typical coal layer complexes in the Czech part of the Upper Silesian Basin: Ostrava layers and Karvina layers. Nowadays, this basin is the only pit coal producing area in the CR. This area has a big potential for enhanced coal-bed methane recovery. The Carboniferous filling of Upper Silesian Basin is mostly covered by Neogene sediments and Carpathian flysch.

The general assessment of the sedimentary basins described above shows that all the three generally recognized options for geological storage of CO_2 (deep saline aquifers, hydrocarbon fields and unmined coal seams) are available on the Czech territory.

5. Storage options

5.1. Aquifers

5.1.1. General description

Regarding aquifers, the attention was aimed at vertically closed structures with sufficient sealing and significant pore volume capacity. Altogether, 22 potentially suitable structures were identified, 17 of them in the Carpathians (eastern part of the country) and 5 in sedimentary basins of the Bohemian Massif. Due to the long-term hydrocarbon exploration, the knowledge of Carpathian structures and their properties is much better than that one of the Bohemian Massif aquifers.

The geographical distribution of the structures considered is shown in Fig. 5.

The Carpathian aquifers are situated in the Carpathian Foredeep (Vlkoš – Lobodice, Mušov, Drnholec, Iváň, Vlasatice) and in the Flysch Zone (Koryčany, Osvětimany – Stupava, Zdounky, Bařice, Rusava, Kozlovice – Lhotka, Frýdlant nad Ostravicí, Vyšní Lhoty – Morávka, Mikulov, Nosislav – Nikolčice, Kobeřice, Kobylí). Promising structures were selected on the base of a former study aimed at identification of aquifers suitable for underground natural gas storage sites (Müller et al., 2000).

Reservoir rocks of the Foredeep aquifers are Lower Miocene sandstones while the seal consists of Upper Miocene claystones. In the Flysch Zone, aquifers are situated mainly in Miocene sandstones except for the structures of Kobylí (Paleocene and Miocene sandstones), Mikulov (Jurassic limestones) and 3 structures in the North (Kozlovice – Lhotka, Frýdlant nad Ostravicí, Vyšní Lhoty – Morávka) where Upper Carboniferous and Miocene sandstones appear. Carpathian Flysch nappes (with claystone layers) form structure sealing in all cases.

The Bohemian Massif aquifers (Žatec, Roudnice, Mnichovo Hradiště, Nová Paka, Police) are situated in Permian-Carboniferous Central Bohemian and Lower Silesian basins, partly covered by thick sediments of the Bohemian Cretaceous Basin. Reservoir rocks are mainly Upper Carboniferous (Stephanian) sandstones and arcoses while the seal is usually formed by overlying Lower Permian (Autunian) claystones. The structures are quite complicated and information about their properties is lacking in large areas. Therefore, the delineation of the aquifers is not so precise as of those ones in the Carpathians and the calculated storage capacities must be considered as rough estimates only. On the other hand, the geographical position of Bohemian aquifers (close to the biggest CO_2 emission sources) is very suitable from the CO_2 storage point of view.

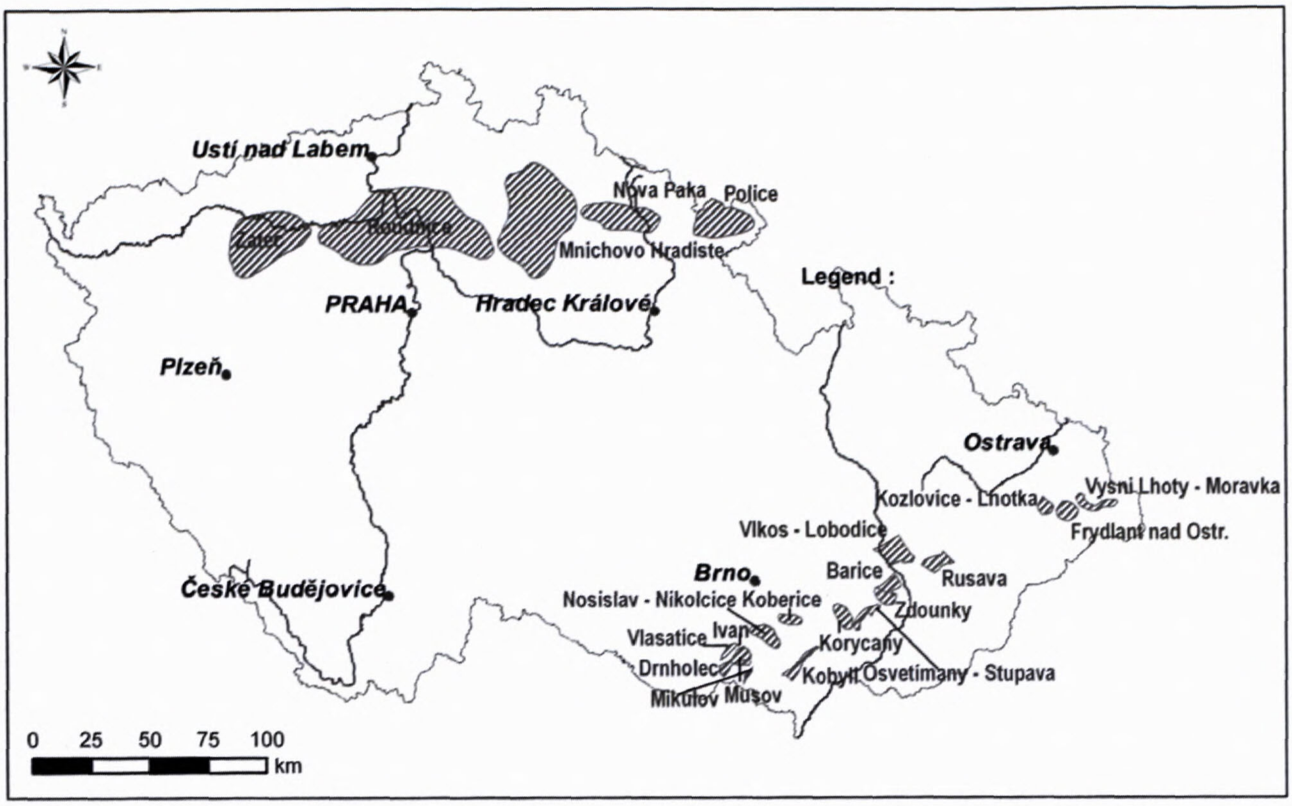

Fig. 5 Geographical distribution of aquifers suitable for geological storage of CO2 in the Czech Republic

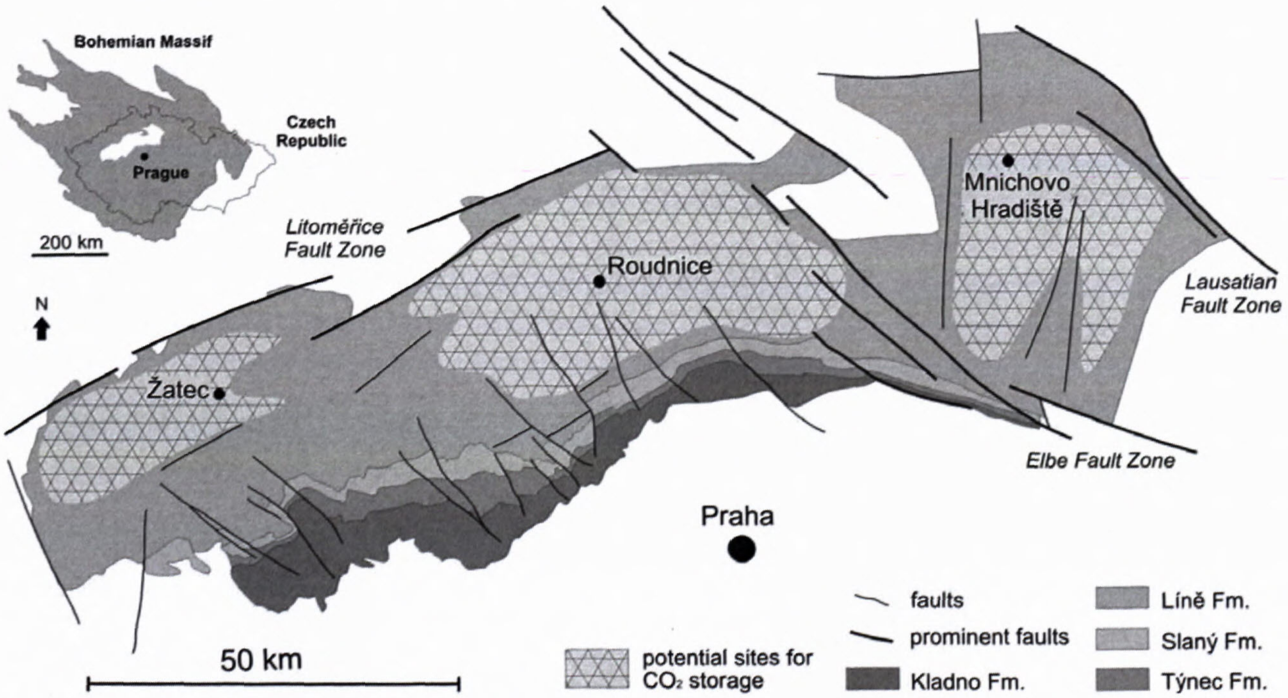

Fig. 6 Simplified and uncovered (Cretaceous, Tertiary) geological map of the Central Bohemian basins (Žatec, Roudnice, Mnichovo Hradiště) with potential sites for CO2 storage

5.1.2. Estimated storage capacity

The storage capacity calculations were based on the volumetric approach. Structure area, average thickness and average porosity were used for pore volume determination, according to the formula (e. g. Brook et al., 2003; Bachu et al., 2007; Bachu, 2008):

$$M_{CO2} = S * t * p * \rho_{CO2} * (1 - S_w) * RF,$$

where M_{CO2} is the effective CO_2 storage capacity, S – area, t – average thickness of aquifer layers, p – average porosity of aquifer layers, ρ_{CO2} – CO_2 density under aquifer conditions (depends on pressure and temperature), S_w – irreducible water saturation, RF – recovery factor (capacity coefficient)

Porosity values used for the calculations were derived from well-log data available. In the Carpathians, the porosity ranges from 5 to 20 %, while in the Bohemian Massif it is considerably lower (up to 6 %, considering the complex structure of the layers). The average CO_2 density value of 630 kg/m^3 (corresponding to the typical pressure and temperature conditions of the aquifers) was used for all structures. The recovery factor used for calculation of the effective storage volume was 6 % for Bohemian regional aquifers and 40 % for Carpathian structures.

The list and main parameters of the aquifers considered is shown in Table 5. The total storage capacity has been assessed at about 2863 Mt CO_2. This means that aquifer structures represent the most important CO_2 storage option in the Czech Republic.

5.2. Hydrocarbon fields

5.2.1. Exploration and production history, stratigraphy, distribution, Ultimate Recovery

Hydrocarbon exploration history in the CR started in 1900 when the first well called "Helena" was finished. This well was located in the Carpathian Flysch Zone (Bohuslavice nad Vláří) and reached a depth of 450 m with some gas shows. In the Vienna Basin (near Hodonín), another well was drilled in the same year (final depth 217 m, gas and oil shows recognized). The first really positive well was finished near Slavkov (Carpathian Flysch Zone) in 1908 and produced gas from 500 m depth for a local sugar factory until 1920. The first oil reservoir was opened in 1920 in the Vienna Basin (near Hodonín). The first production well produced oil from 313 - 338 m depth and the daily production of the field was about 80 t in 1925 (Bednaříková et al., 1984).

At present, there are more than 40 oil and gas producing fields in the CR, registered by Czech Geological Survey - Geofond. All of them are located in the eastern part of the CR, in the Carpathians (Vienna Basin, Carpathian Foredeep, Carpathian Flysch Zone). From the stratigraphic point of view, Miocene sediments represent the reservoir rocks in all these areas. In the Carpathian Flysch Zone, oil & gas can be found in Mesozoic and Paleozoic sediments as well. In some cases, hydrocarbon reservoirs are situated in weathered crystalline complexes.

Some of the reservoirs are depleted, especially the shallow structures in the Vienna Basin. Deeper structures in the Vienna Basin are still producing, as e.g. the fields Hrušky (oil and gas), Týnec (oil), Lanžhot (oil), Poddvorov (oil and gas), Vracov (oil), Lužice (oil), Poštorná (oil) and Prušánky (oil and gas). Most of the structures in the Vienna Basin represent tectonic traps.

Most of the gas reservoirs located in the Carpathian Foredeep are depleted and some of them have been transformed into natural gas underground storage sites (e.g. Dolní Dunajovice).

Nowadays, the most important producing oil and gas reservoirs are located in the Carpathian Flysch Zone. The majority of Czech oil production is coming from the Dambořice – Uhřice and Žarošice fields (tectonic traps in combination with elevation). Production layers are sediments building the basement of Flysch nappes, i.e. Jurassic and Paleozoic. There are also some small gas fields in Miocene sediments (Ždánice area) and small oil reservoirs in the crystalline basement (Ždánice, Lubná - Kostelany) there. In 2004, the Janovice gas structure (Miocene – tectonic trap) in the northern part of the Flysch Zone was reopened.

The fields Dambořice – Uhřice and Žarošice produced both together 267 thousand m^3 of oil in the year 2006, it is about 86 % of the cumulative oil production of the Czech Republic (311 th. m^3 in 2006). The main gas producing field (except CBM production from Upper Silesian Basin) is now the Kloboučky field located in Ždánice area, Carpathian Flysch Zone, with production about 20 millions m^3 in the year 2006 (cumulative national gas production including CBM in 2006 was 222 mill. m^3). Domestic production of crude oil and natural gas in the Czech Republic represents only 3 %, resp. 2 % of the domestic consumption (oil - 9,067 th. m^3, gas - 9,804 mill. m^3 in 2006; Czech Statistical Office, 2008).

5.2.2. EOR possibilities

The first EOR attempts (using various media) in the CR were performed in the 1960s and 1970s. The most important was the water-flooding into oil reservoirs of the Hrusky field. During the years 1964 – 1974 more then 1 million m^3 of water has been injected. The EOR effect has been calculated at about 12 %. Nowadays, the Dambořice – Uhřice oil & gas field is being transformed into a natural gas storage and natural gas injection helps to increase the oil production. Unfortunately, the domestic operator (MND) does not publish more detailed information.

Nevertheless, many of the partly depleted oil fields in the Vienna Basin and the Carpathian Flysch Zone are suitable for CO_2-EOR. Their operator shows interest in using this technology in future but, until now, no suitable source of CO_2 has been available.

5.2.3. Estimated storage capacity

For the calculation of the CO_2 storage capacity of oil and gas reservoirs, 6 major hydrocarbon fields were considered. 4 of them are situated in the Carpathian Flysch Zone (Lubná –Kostelany, Ždánice, Dambořice – Uhřice, Žarošice) while the 2 remaining belong to the Vienna Basin (Hrušky and Poddvorov). The size of other reservoirs is too small and their storage capacity can be regarded as negligible.

The storage capacity calculations were based on the volumetric approach. The basic assumption is that the theoretical capacity for CO_2 storage in hydrocarbon reservoirs equals to the volume previously occupied by the produced oil and gas (Gozalpour et al., 2005, Bachu et al., 2007). To determine this volume, the Ultimate

Tab. 5 – Selected aquifers of the Czech Republic and their basic parameters

Structure name	Stratigraphic unit	Lithology	Depth of structure top [m]	CO_2 storage capacity [Mt]
Kobeřice	Miocene	sandstone	1 300	43.1
Nosislav - Nikolčice	Miocene	sandstone	945	82.7
Vlasatice	Miocene	sandstone	930	4.3
Mušov	Miocene	sandstone	880	12.1
Iváň	Miocene	sandstone	825	81.6
Drnholec	Jurassic	limestone	880	5.3
Mikulov	Miocene	sandstone	1 005	31.0
Kobylí	Paleocene - Miocene	sandstone	1 100	317.5
Zdounky	Miocene	sandstone	1 115	17.1
Bařice	Miocene	sandstone	1 115	56.4
Vlkoš - Lobodice	Miocene	sandstone	800	270.6
Rusava	Miocene	sandstone	1 055	66.0
Kozlovice - Lhotka	Upper Carboniferous - Miocene	sandstone	815	48.9
Frýdlant nad Ostravicí	Upper Carboniferous - Miocene	sandstone	925	62.7
Vyšní Lhoty - Morávka	Upper Carboniferous - Miocene	sandstone	965	35.0
Koryčany	Miocene	sandstone	1 365	10.6
Osvětimany - Stupava	Miocene	sandstone	1 585	34.0
Žatec	Upper Carboniferous	sandstone (arcose)	950	450.0
Roudnice	Upper Carboniferous	sandstone (arcose)	830	872.0
Mnichovo Hradiště	Upper Carboniferous	sandstone (arcose)	1 100	274.0
Nová Paka	Upper Carboniferous	sandstone (arcose)	900	50.0
Police	Upper Carboniferous	sandstone (arcose)	1 200	38.0
Total				**2 862.9**

Tab. 6 – Major hydrocarbon fields of the Czech Republic and their basic parameters

Field name	Stratigraphic unit	Lithology	Depth [m]	Ultimate Recovery – oil [mill m^3]	Ultimate Recovery – gas [mill m^3]	CO_2 storage capacity [Mt]
Hrušky	Miocene – Badenian	sandstone	1 320	1.82	2 099	14.1
Poddvorov	Miocene – Sarmatian	sandstone	930	0.48	850	5.3
Lubná –Kostelany	Cambrian	granite	1 300	0.14	208	1.4
Ždánice	Cambrian & Miocene	granite, sandstone	750	0.76	628	4.1
Dambořice – Uhřice	Carboniferous & Jurassic	sandstone, carbonates	1 900	2.39	491	4.5
Žarošice	Jurassic	carbonates	1 680	0.84	453	3.3
Total				**6.43**	**4 729**	**32.7**

Recovery /UR/ figures (i.e. previous production + proven recoverable reserves), both for oil and for gas, were used. In the case of oil, the 1:1 ratio was used to convert the volume of UR oil into reservoir pore volume ready to store CO_2. In the case of natural gas, the Bg factor (ratio between gas volume under surface conditions and its volume under reservoir conditions) was used to calculate the original pore volume occupied by natural gas in the reservoir. The average value of Bg = 0.0095 (kindly recommended by RWE-Transgas, the domestic natural gas storage operator) was used for the calculations. To convert the calculated pore volume into CO_2 storage capacity, the average CO_2 density value of 630 kg/m^3 (corresponding to the typical pressure and temperature conditions of the reservoirs) was used for all structures.

The list and main parameters of the structures considered is shown in Table 6. The total storage capacity of the 6 major fields has been assessed at about 32.7 Mt CO_2. This means that hydrocarbon structures do not play a significant role as potential CO_2 storage site but, on the other hand, they represent an interesting potential from the EOR point of view.

The geographical distribution of the oil & gas fields considered is shown in Fig. 6.

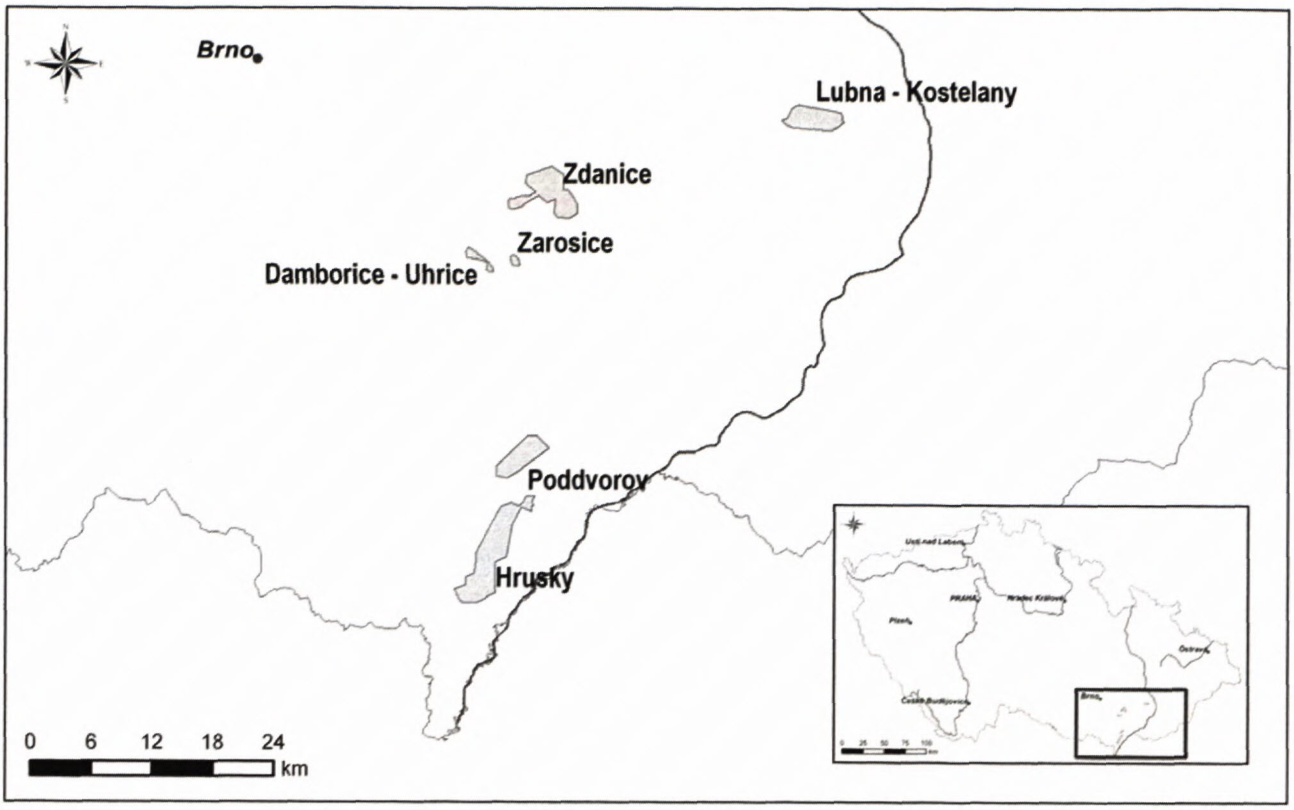

Fig. 7 Location of major hydrocarbon fields of the Czech Republic

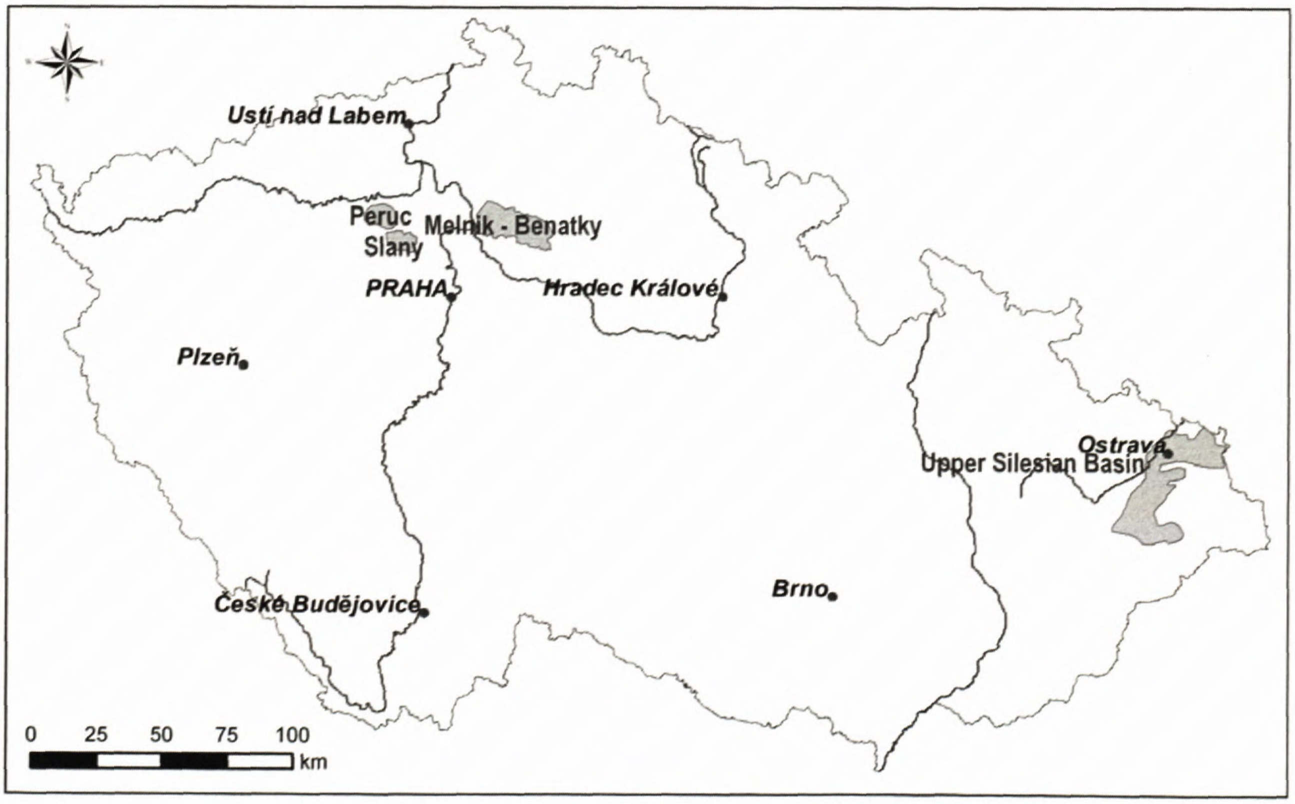

Fig. 8 Location of major coal measures with ECBMR potential in the Czech Republic

Tab. 7 Major coal measures with ECBMR potential in the Czech Republic and their basic parameters

Name	Stratigraphy	Depth of structure top [m]	Total PGIP* [mill. m^3]	CO_2 storage capacity [Mt]
Upper Silesian Basin	Carboniferous - Namurian	600	100 000	380,0
Slaný	Carboniferous – Westphalian C	900	1 778	6.8
Peruc	Carboniferous – Westphalian C	1200	2 840	10.8
Mělník - Benátky	Carboniferous – Westphalian C	600	2 670	10.1
Total				**407,7**

*PGIP = producible gas in place

5.3. Coal measures

History of coal mining in the CR is very rich but the majority of Czech pit coal collieries has been recently closed. At present, pit coal collieries are located in the Upper Silesian Basin only. For the purposes of CO_2 storage, however, the unmined pit coal measures are interesting, especially due to the enhanced coal bed methane recovery (ECBMR) possibilities. Such structures can be found in large parts of the Upper Silesian Basin and in Permian-Carboniferous Central Bohemian Basins (see Fig. 7).

Upper Silesian Basin (USB) is a large and complex paralic – limnic sedimentary structure stretching from NE part of Czechia far into Poland. In the northern part of the Czech portion of USB, extensive coal mining activity has been carried out while the southern and south-eastern parts (deeper and partly covered by Carpathian Flysch) remained unmined. Coal layers are of Namurian and Westphalian age; the overlying Miocene sediments as well as the Flysch nappes can be considered as seals. For the purposes of this study, the basin was handled as one structure. The estimation for the whole area of the Czech part of USB is at minimum 100 milliards (US billions) m^3 CBM (Durica et al, 2006). To be able to refine the first rough CO_2 storage capacity estimate and assess the ECBMR potential, it will be necessary to divide the basin into several parts according to geological conditions. This work is planned to be done within follow-up research projects.

The Central Bohemian structures (Slaný, Peruc, Mělník – Benátky) represent typical limnic coal basins. Substantial coal layers are of Westphalian age and the seal is composed of claystones (Westphalian to Stephanian sedimentation). All of these 3 structures were subject of geophysical and geological exploration in the 1970s and 1980s (e.g. Žbánek et al. 1978, 1988 & 1991). However, the plans to open new pit coal collieries in these areas have not become reality.

The storage volume calculations were based on the assessments of total producible gas in place (PGIP) that were made within the framework of coal bed methane studies between 1990 – 2003 (EPA report, 1992; Bódi et al., 1992; Hemza, 2000; Ďurica & Müller, 2003; Ďurica et al. 2006), using the formula:

$$Q = M * p * k * c$$

/where Q = PGIP (m^3), M = pure coal mass (t), p = real methane content (m^3 per tonne of coal), k = recovery factor, c = completion factor/. A simple exchange ratio 1:2/i.e. 1 molecule of CH_4 is replaced by 2 molecules of CO_2, suggested e.g. by van Bergen & Wildenborg (2002)/ and so called CO_2 normal condition density was used for the rough estimations of CO_2 storage capacities.

The list and main parameters of the structures considered are shown in Table 7. The total storage capacity of the selected unmined coal measures has been assessed at about 408 Mt CO_2. This volume represents an interesting storage potential, especially if the ECBMR possibilities are taken into account.

6. First estimate of country-wide storage capacity

Based on the results described in Chapter 5, the first rough estimate of CO_2 storage capacity in geological structures of the CR was made (see Tab. 8).

Compared with the CO_2 emission data (82 Mt/yr from stationary industrial point sources, see Tab. 3) and taking into account the 1.3 capture loss coefficient, the selected geological structures would hold all industrial CO_2 emissions of the country produced during 30.9 years (provided the emission level of 2005-7 will not change).

Tab. 8 Overview of CO_2 storage options in the Czech Republic

Structure type	Total CO_2 storage capacity [Mt]
Aquifers	2 862.9
Hydrocarbon fields	32.7
Coal measures	407,7
Total	**3 303.3**

7. Conclusions

Despite the fact that protection of the climate system of the Earth is a top-priority environmental issue in the Czech Republic, the public awareness of the CO_2 capture and storage (CCS) technology is generally low. Until now, the research pioneers (especially the Czech Geological Survey and a few others) were able to start building the awareness of CCS as a viable climate change mitigation option among environmental policy decision makers (Ministry of Environment, etc.) and the geological research community. This long-term effort is, however, at its beginning and much work has still to be done.

The first estimate of country-wide CO_2 storage capacity, compiled within this study, is one of the most important steps on this way. The calculated volume of ca. 3300 Mt CO_2 shows that geological structures are able to hold the entire volume of the CO_2 industrial emissions for more than 3 decades. Another positive conclusion of the study is that prospective storage structures could be found relatively close to the biggest CO_2 emission sources (e.g. aquifers of the Central Bohemian Basins, see chapter 5.1).

Aquifers represent an overwhelming majority (86.7 %) of the storage capacity but in some cases (especially in the Bohemian Massif) the level of knowledge of the structures is quite low and additional data would be needed before a CO_2 storage project might be started. The share of coal measures (12.3 %) and hydrocarbon fields (1.0 %) in the total storage capacity is quite low. These options, however, are interesting from the economical point of view because they might be connected with enhanced hydrocarbon recovery.

The Czech National Program to Abate the Climate Change Impacts in the Czech Republic declares ambitious emission reduction targets, exceeding the Kyoto protocol commitments - to reduce CO_2 emissions per capita by 30 % until 2020 compared to 2000, to reduce total aggregate CO_2 emissions by 25 % in 2020 compared to 2000 and to keep at the commenced trend to 2030. Considering these ambitions, it is clear that development and application of new advanced technologies, including CO_2 capture and geological storage, is inevitable. To prepare a reliable ground for political decisions, further research in the area of geological storage of CO_2 is needed, incl. selection of the most prospective sites, case studies and potentially a pilot project.

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CO_2 Emissions and Geological Storage Options in Bulgaria

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Abstract. In CO_2 emissions inventory for Bulgaria are included all 42 large industrial sources (>0.1 Mt/year). The Energy sector gives the largest portion of country CO_2 emissions - 33.7 Mt/y or almost 65 %. The thermal power plants produced 25.3 Mt/y (48.5 %) and combined power & heating plants – 8.4 Mt/y (16.1 %). In the country there are 4 zones with a high concentration of industrial CO_2 sources and emissions - they produced totally 46 Mt/y CO_2 which equates to 88 % of all industrial CO_2 emissions.

The large presence of thick sedimentary succession and the high exploration rate of Northern Bulgaria are favourable preconditions for assessment of CO_2 storage opportunities and development of CO_2 storage activities. In Southern Bulgaria the sedimentary spreading is restricted in area and thickness and related with numerous small intra-mountain young basins.

The presented Bulgarian CO_2 storage capacity estimation is based on large data base, including mainly original seismic and borehole results, integrated with our knowledge on the subsurface and with a unified way of calculating the capacity in HC fields, aquifers and coal beds, accepted in the frame of EU GeoCapacity project.

The largest capacity of potential CO_2 storage options in Bulgaria related with aquifers, coal fields have considerably less opportunities, while the possibilities to use depleted hydrocarbon fields practically there are not.

The main problem for the CO_2 geological storage in Bulgarian is that the selected and estimated country storage options are located far from major CO_2 sources. Main storage capacities related to Northern Bulgaria, while the main concentrations of country industrial CO_2 emissions are mainly in Southern Bulgaria.

Key words: Bulgaria, CO_2 emissions, Geological storage options, Storage capacity

Introduction

Bulgaria is a small country in SE Europe - occupies 110 994 km^2 of territory on the Balkan Peninsula and has population about 8 millions. According to Kyoto Agreement ratified in 2002, Bulgaria is responsible to reduce CO_2 equivalent emissions with 8 % as compared to the base 1988 year, when were recorded 100.28 Mt/year. Reduction of 8 % means 8.02 Mt, so the Kyoto limit of 92.261 Mt/year CO_2 equivalent emissions should be achieved in the 2008 – 2012 period.

The industrial collapse in the country after democratic changes in 1990 has reduced significantly the produced CO2 emissions and they became vastly less than the fixed Kyoto limit. However, if the Government intentions to turn Bulgaria into energy centre on the Balkan Peninsula take place, the emissions from new build thermal power and industrial plants will increase significantly and may reach and exceed the Kyoto limit of 92 Mt/year.

The large presence of thick sedimentary succession in Bulgaria and the high exploration rate of Northern Bulgaria are favourable preconditions for assessment of CO_2 storage opportunities and development of CO_2 storage activities.

The first estimation of CO_2 storage capacity for Bulgaria was made as a part of the CASTOR project (2004-2005). This assessment has been updated, enlarged and elaborated in the frame of EU GeoCapacity project (2006-2008).

CO_2 emissions inventory

The industrial CO_2 emissions in Bulgaria from all 42 large point sources (>0.1 Mt/year) are 52.2 Mt/y (estimation in 2006). Total number of monitored combustion plants (CP) in the country is larger, about 130. However, most of them have yearly CO_2 emissions less then 0.1 Mt/y and their total CO_2 amount is not more than 4-5 % of annual industrial CO2 production in the country. Fig. 1 shows the distribution of all 42 large industrial CO_2 sources included in the estimation and the basic concentrations of CO2 emissions in Bulgaria.

Generally 7 industrial groups of CO2 emissions exist in the country. They are: I - Power (5 plants); II - Power & Heating (13 plants); III - Refineries (1); IV - Iron & Steel (4 plants); V - Cement (5 plants); VI - Ammonia & Chemicals (10 plants) and VII – Others, mainly lime & ceramics (4 plants). Their contribution to country CO_2 industrial emissions is seen from Fig. 2.

The Energy sector, incorporating the first two groups, gives the largest portion of country CO_2 emissions – 33.7 Mt/y or almost 65 %. The thermal power plants

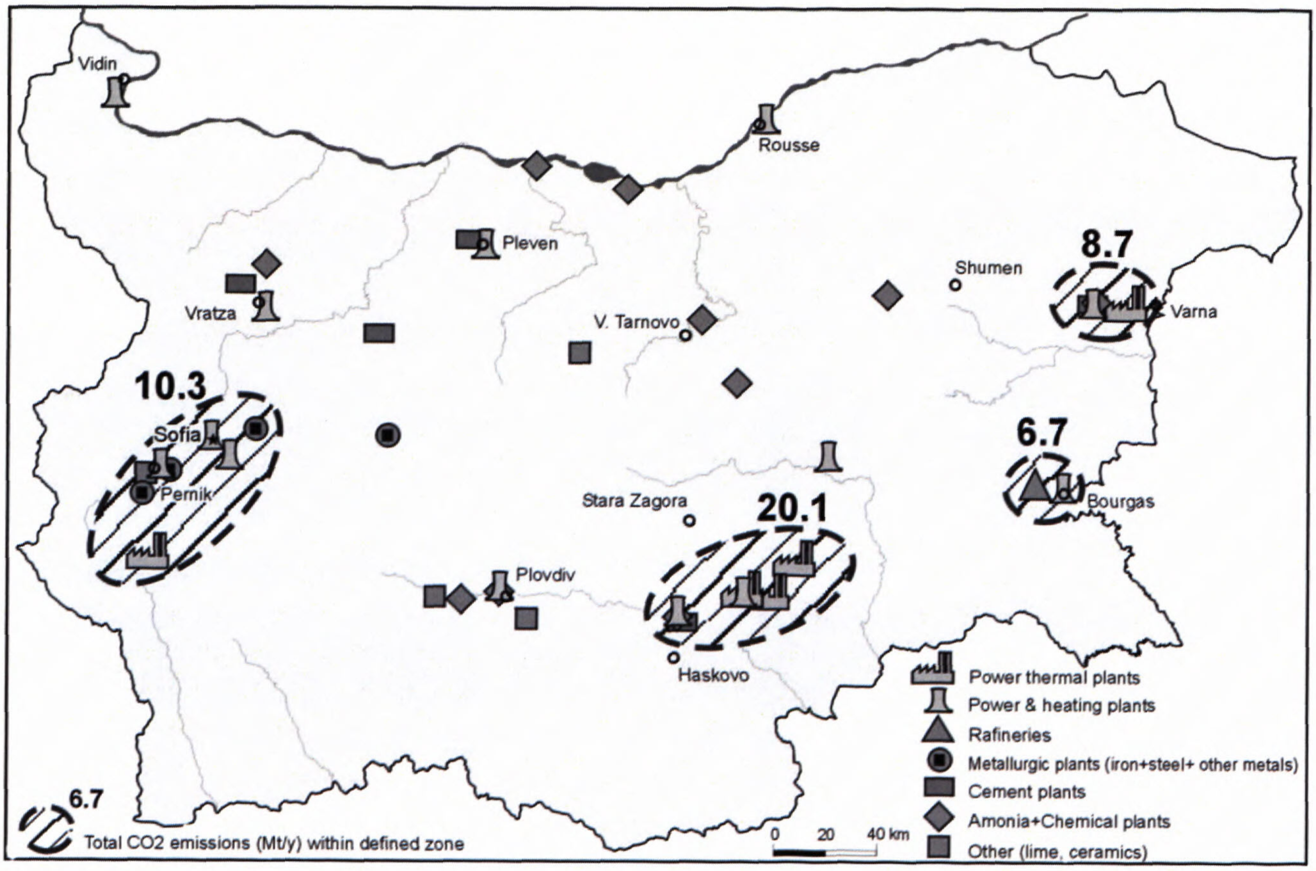


Fig. 1 Distribution of all large industrial CO_2 sources and basic concentrations of CO_2 emissions in Bulgaria.

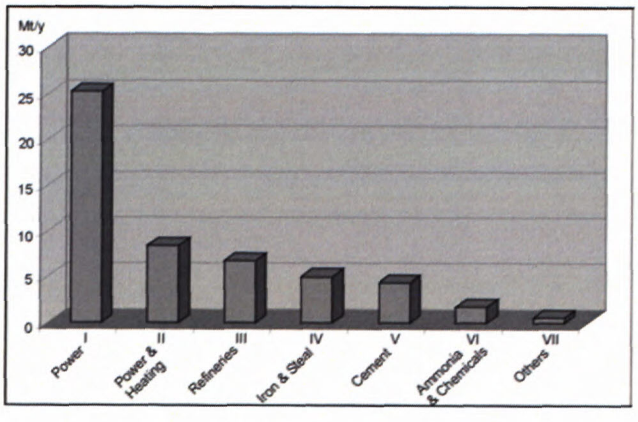


Fig. 2 Contribution of industrial groups to country CO_2 emissions.

produced 25.3 Mt/y (48.5 %) and combined power & heating plants – 8.4 Mt/y (16.1 %). For thermal power plants, the basic fuel is coal from local mines or imported, while the combined power & heating plants use mainly gas.

The largest CO_2 emitters in the country are all 5 thermal power plants, the refinery near to Bourgas and the steel plant near to Sofia (Fig. 1). They produced totally 36.7 Mt/y CO_2 or 70 % from country CO_2 industrial emissions.

In Bulgaria there are 4 zones with a high concentration of industrial CO_2 sources and emissions - they produced totally 46 Mt/y CO_2 which equates to 88 % of all country CO_2 emissions (Fig. 1). The highest CO_2 concentration (20.1 Mt/y or 38.5 %) is located in the middle of Southern Bulgaria and related with the largest producing coal field "Maritza East". This zone comprises 3 of the largest thermal power plants, as well as some other big industrial emitters. The other 3 zones related with Sofia–Pernik, Varna and Bourgas areas.

In general for the country the number of larger CO_2 emitters and the amount of produced CO_2 are much bigger in Southern Bulgarian (Fig. 1).

Geological settings

Bulgaria has an extensively varied and complex geological structure (Atanasov et al. 1984; Georgiev & Dabovski, 1997). Several major tectonic units are recognized, they are: Moesian platform, Alpine thrust-folded belt with Tertiary foredeep (named Kamchija depression), Sakar and Strandzha orogenic zones and a system of small syn- to post-orogenic Tertiary extensional basins (Figs 3, 4, 5, 6, 7). In addition, the offshore area covers and some parts of the western periphery of the Western Black Sea basin.

Two branches of Alpine orogenic belt and their foreland can be seen in Bulgaria (Fig. 3). The northern branch, represented by the Balkanides (Balkan and Forebalkan), crosses the country in the middle from west to east; Moesian platform is foreland. The southern branch comprises the Kraishtides, Srednogorie and Rhodope massif and could be considered as a pre-Alpine basement of the Balkanides (Georgiev & Dabovski, 1997).

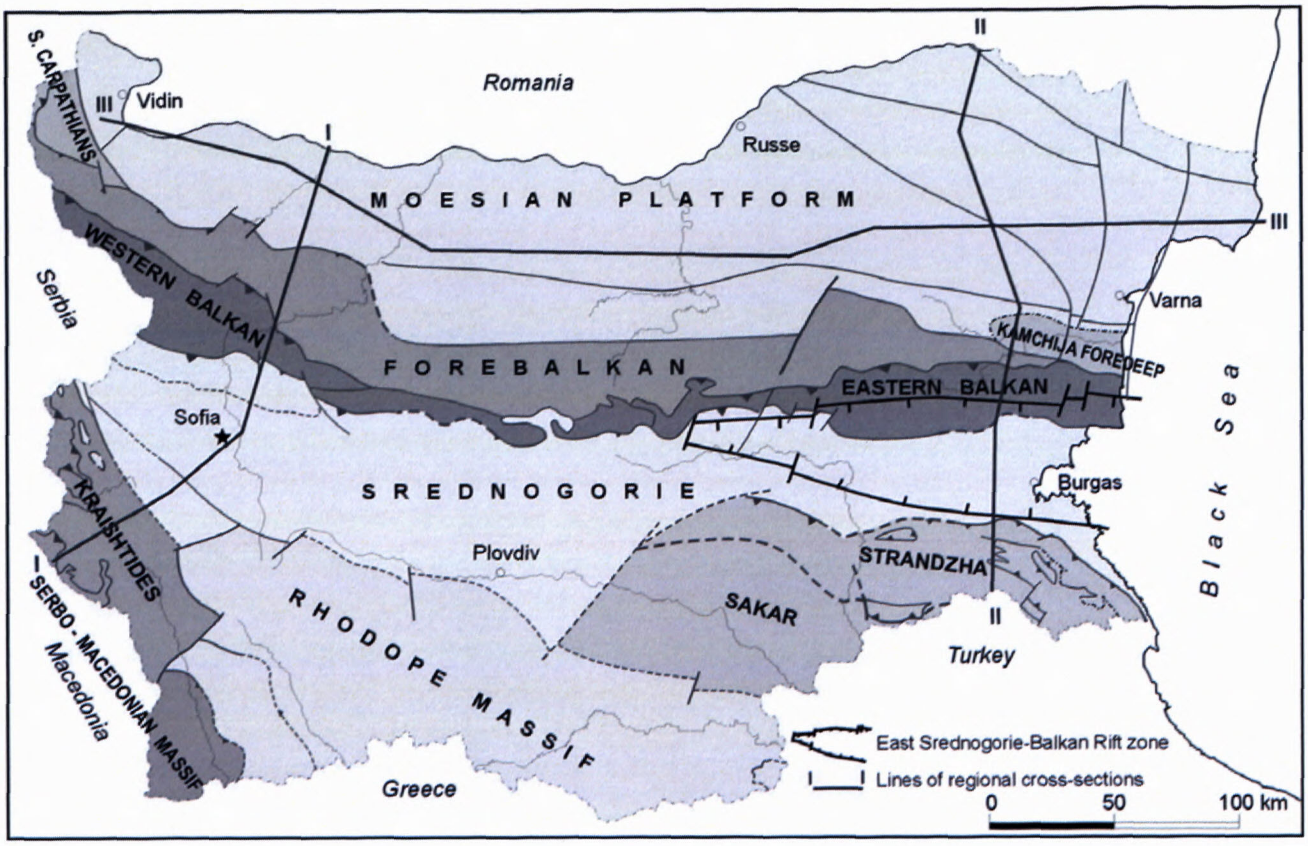


Fig. 3 Major tectonic units in Bulgaria (by Georgiev & Dabovski, 1997 – modified).

The Moesian Platform, which southern part extended in Northern Bulgaria, forming the foreland of the Balkan thrust-folded belt, is composed of up to 4-5 km thick relatively un-deformed, dominantly shallow-marine Mesozoic sediments, that rest on a gently folded Palaeozoic basement (Figs 4, 5, 6, 7). Totally, the Phanerozoic sedimentary succession in Moesian platform has a thickness of 4-13 km. Major unconformities, occurring at the base of the Triassic, Jurassic, Upper Cretaceous and Eocene (Fig. 8), are related to major compressional events within the Alpine thrust belt.

Five sedimentary zones (tectonic units) with increased sedimentary thickness are present in Bulgarian part of Moesian platform (Fig. 4):

- The Southern Moesian platform margin (SMPM) subsided with accelerates rates during the Jurassic-Early Cretaceous time (Figs 5, 6, 8).
- The Lom basin has a similar evolution as SMPM, but the accelerate subsidence in it continuing during the Tertiary also (Figs 3, 4, 5). By these features the Lom basin is considered lately as a westernmost zone of SMPM (Georgiev & Dabovski - 1997).
- The Alexandria basin, which small SE part is spread in Bulgaria, developed during the Middle-Late Triassic.
- The Varna basin actually represent the eastern slope of North Bulgarian arch, which was involved in accelerate subsidence mainly during the Triassic and Late Cretaceous – Tertiary (Figs 4, 7).
- The Kamchija basin corresponds to a post-Middle Eocene foredeep that is filled with late Eocene-Oligocene and Neogene clastics and clays. Towards the East, this foredeep deepens and merges offshore with the Western Black Sea basin.

The northern branch of Alpine orogenic belt (Balkan–Forebalkan) consists of a stack of dominantly north-verging thrust sheets (Figs 3, 5, 6), formed during long displaying multiphase compression, which began in the Late Triassic and culminated toward the end of the Early Cretaceous and to the end of the early Middle Eocene (Georgiev & Dabovski, 1997).

The Balkan (Stara Planina) thrust-folded belt is a major tectonic unit in Bulgaria, which is a comparatively narrow stripe, consisting of strongly folded and northward over-thrusted Mesozoic and early Tertiary sediments (Figs 3, 5, 6). The Western Balkan is composed mainly by Paleozoic and Triassic mixed sedimentary, metamorphic and magmatic sequences, the tectonic style is higher (Figs 3, 5). While, in the Eastern Balkan dominated the Upper Cretaceous and Paleogene sedimentary sequences, the tectonic style is lower (Figs 3, 6, 8).

The Forebalkan is the northernmost unit of the Northern Alpine orogenic belt, through which the structural transition between Balkan and Moesian platform takes place (Figs 3, 5, 6). Tectonically this unit is closer to Balkan, only it has lower style. However, by sedimentary succession it is closer to Moesian platform, what means that it is the southernmost strip of SMPM, which is folded by northward-directed orogeny in the Balkan. A series of en-echelon narrow folds were thrust over the SMPM.

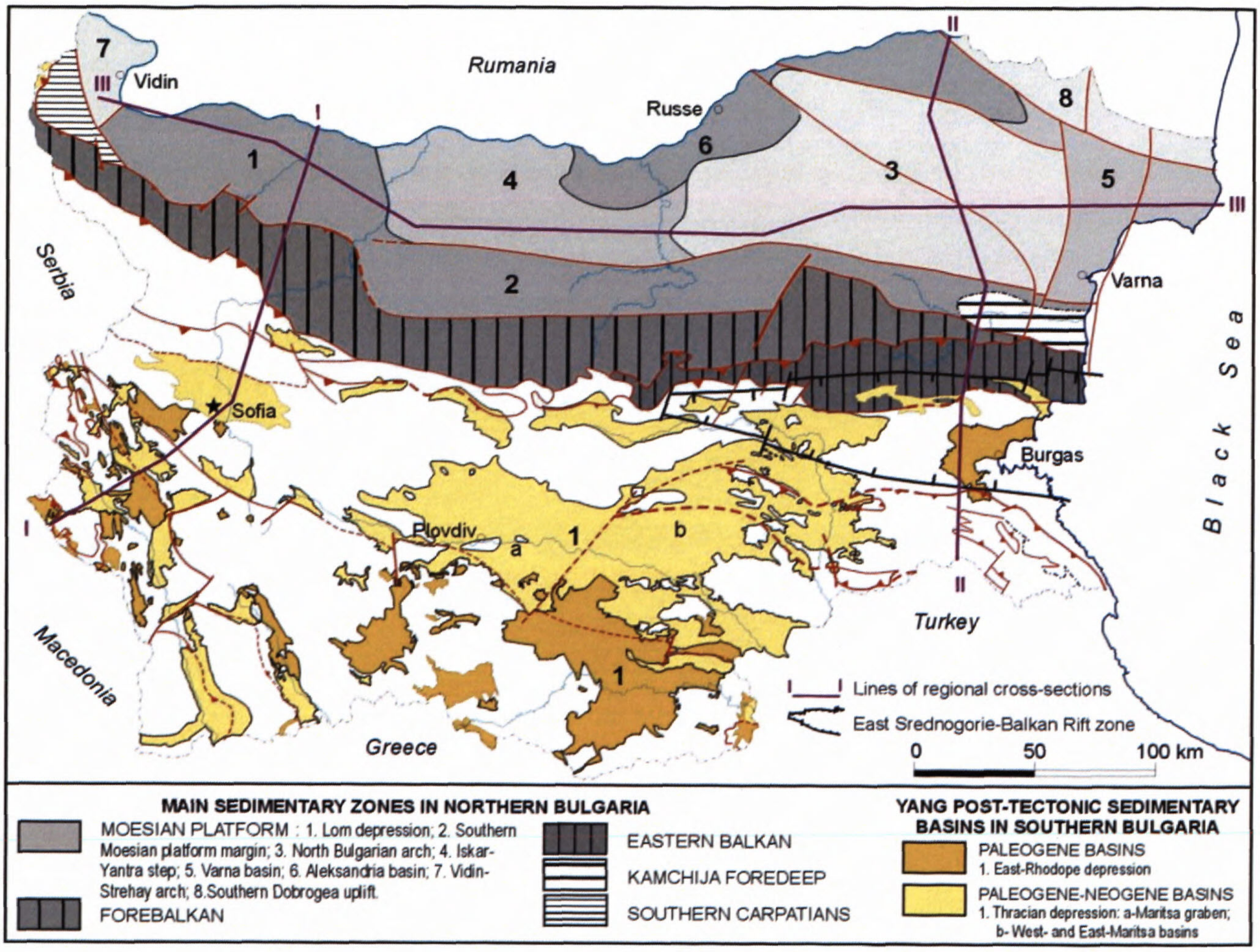


Fig. 4 Main sedimentary basins and zones in Bulgaria (composed by Georgiev & Dabovski, 2007 – no published).

In the Forebalkan are distinguished three longitudinal units by differences in sedimentary succession, tectonic and morphologic features (Georgiev et al., 1993). They are separated by transverse oriented small depressions. The Western Forebalkan is typical post-platform orogen (Bokov, 1968), made-up during the Illyrian tectonic phase in Middle Eocene. In the Central Forebalkan a very thick (up to 3 km and more) Upper Jurassic flysch sequence controlled the thrust-tectonic processes in Mid Cretaceous (Austrian phase) and Middle Eocene (Illyrian phase). Eastern Forebalkan is structurally shaped by salt tectonics during mainly the Mid Cretaceous (Austrian phase) in the Upper Triassic evaporates, thick above 1000 m (Georgiev, 1996).

The Rhodope Massif is dominating by high-metamorphic and magmatic rocks. Recent concepts consider it to be made up of several overlapping nappes.

The Srednogorie is separated from the Balkanides to north and from the Rhodope Massif to south by Early Alpine wrench and normal faults. This zone contains two large groups of rocks: the lower one consists mainly of metamorphics (amphibolites, gneisses, gneisses, marbles), the upper one consists of rhythmic volcano-clastic sequences and molasses thick of over 3000 m.

The zone of Kraishtides belongs to southern Alpine orogenic branch in Bulgaria. It is considered by many Bulgarian geologists as a lineament of high ranking folding, wrenching and faulting. This zone is one of the most seismically active on the Balkan Peninsula.

The Strandzha unit is the southernmost, topmost basement-cover nappe of Eastern Bulgaria. Its basement is composed of Precambrian high-grade and Palaeozoic low-grade metamorphic rocks. The sedimentary cover comprises Triassic platform carbonates and Lower-Middle Jurassic sandy-calcareous and shaly-silty series (autochthonous), which are topped by slices of exotic nappes, consisting of Palaeozoic and Triassic deposits (allochthonous).

In Southern Bulgaria the sedimentary spreading is restricted in area and thickness and related with numerous small intra-mountain young basins in the Srednogorie zone, between the Kraistides and the Rhodope and in the Rhodope zone (Figs 4, 5, 6). Only Thracian depression is larger in spreading and sedimentary thickness, which exceeds 800–1000 m in some parts of Maritsa graben and West-Maritsa basin.

In the *East Srednogorie – Balkan rift zone* the thickness of sedimentary succession grow vastly (Figs 4, 6, 8), because several spatially superimposed rift basins developed during the Permian-Early Triassic, Early Jurassic, Late Jurassic (?) and Late Cretaceous (Georgiev et al., 2001).

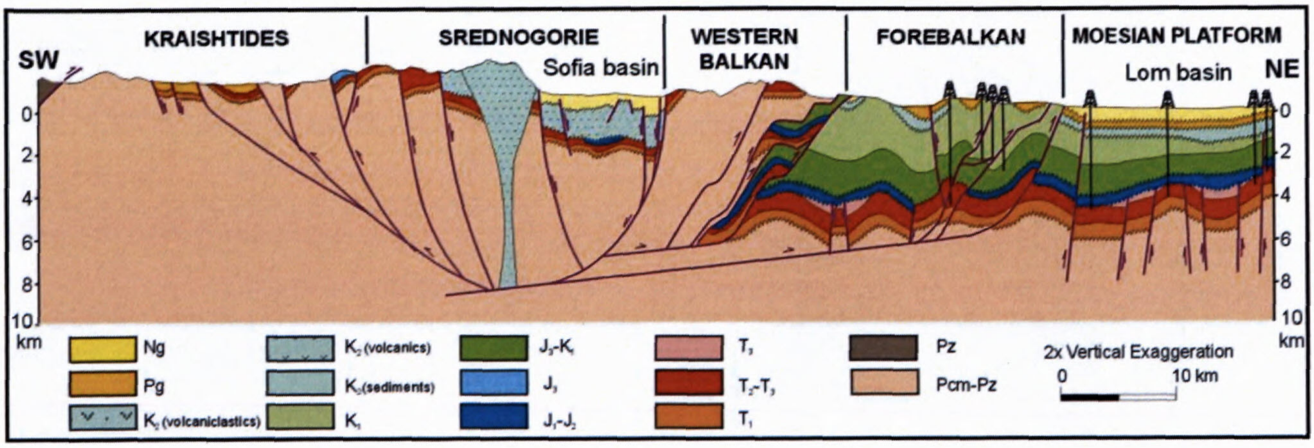


Fig. 5 Regional geological cross-section along line I-I (Figs 3 and 4), giving an overview for the differences in geological structure and sedimentary spreading in western part of Northern and Southern Bulgaria (Georgiev & Dabovski, 2004 in Cavazza et al.–eds., 2004).

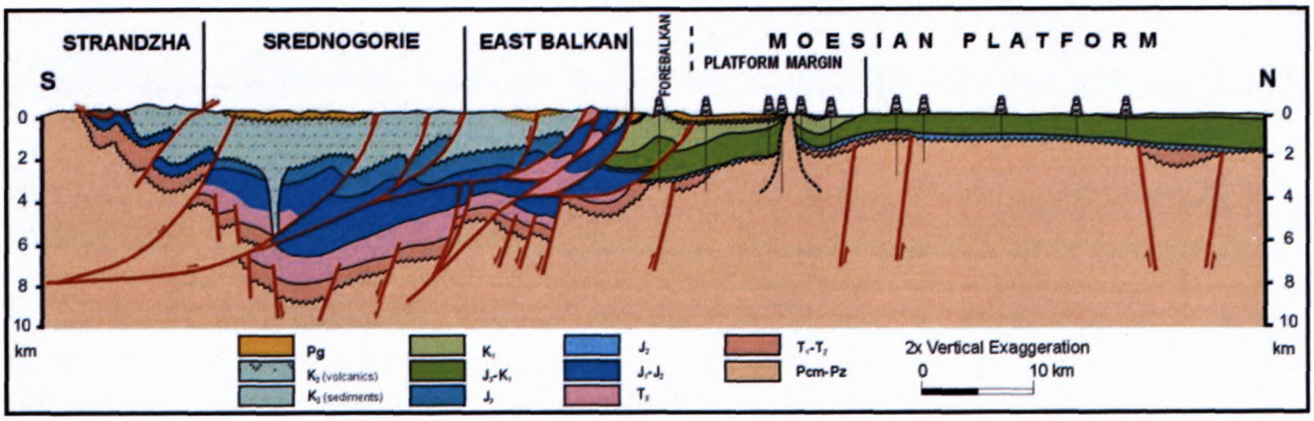


Fig. 6 Regional geological cross-section along line II-II (Figs 3 and 4), giving an overview for the differences in geological structure and sedimentary spreading in eastern part of Northern and Southern Bulgaria (Georgiev et al., 2001).

The Bulgarian offshore covers the easternmost fragments of Moesian platform and Balkanides, as well the western periphery of the Western Black Sea basin and of the young Tertiary Bourgas basin. Most of them have promising sedimentary features for local and zonal spreading of deep saline aquifers.

The seismicity of Bulgarian territory is shown by Fig. 9. The made seismic zoning (Bonchev et al. 1982) is based on a large range of initial geological, geophysical, seismological and other necessary information. The evaluation of seismicity was made by the ability to produce earthquakes of different energetic level depending on the character and intensity of tectonic processes, as well taking in mind the distribution and magnitude of recorded earthquakes.

The expected seismic source zones (SSZ) (Fig. 9) are traced through extrapolation along the earthquake sources of a given magnitude interval, along the zones of the lineaments. Furthermore, they extend also along the intersecting lineament up to the point of its next intersection, within the contour and depth of active layer. It may be assumed that such approach gives the most accurate estimation of expected SSZ on Bulgarian territory.

Recent and current volcanic activity on Bulgarian territory is not marked. However, several stages of volcanic activity in geological evolution were recorded in sedimentary succession. Volcanic manifestation is marked in Late Permian – Early Triassic, Late Cretaceous (Turonian-Santonian), Paleogene (Eocene-Oligocene) and Neogene (by basalt intrusions).

Estimation of CO_2 Geological Storage options

The industrial CO_2 emissions can be captured, transported and stored in suitable underground storage reservoirs. The most promising options to store CO_2 in geological formations are: in empty (depleted) oil and gas fields; in aquifers (deep saline water bearing layers) and in un-mined coal seams.

The presented Bulgarian CO_2 storage capacity estimation (Table 1) is based on large data base, including mainly original seismic and borehole results, integrated with our knowledge on the subsurface and with a unified way of calculating the capacity in HC fields, aquifers and coal beds, accepted in the frame of EU GeoCapacity project.

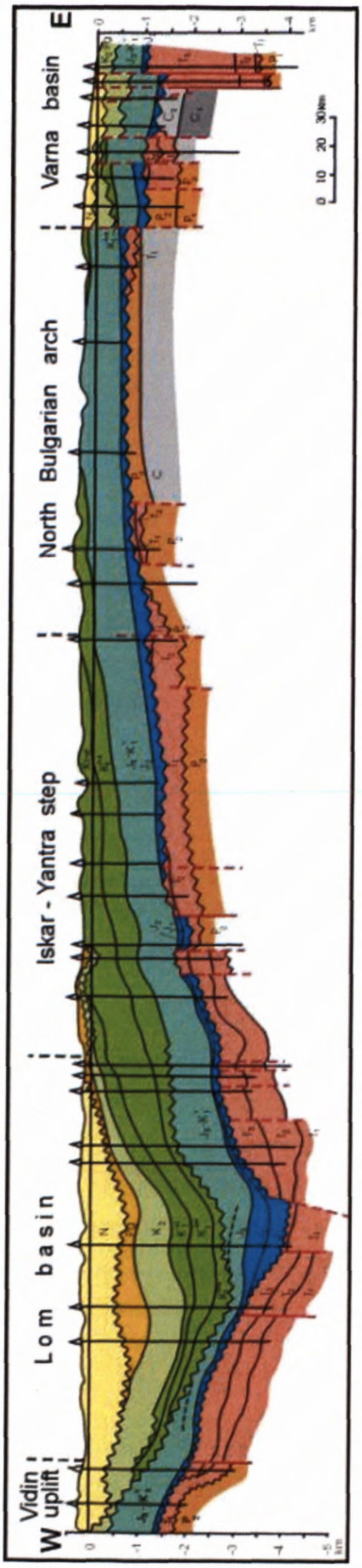


Fig. 7 Regional geological cross-section along line III-III (Figs 3 and 4), giving an overview for the Mesozoic-Tertiary sedimentary thickness variations in the Moesian platform (by Kalinko, ed., 1976 - updated).

Table 1. Capacity of potential CO_2 storage options in Bulgaria

Options	Storage capacity in Mt
Depleted hydrocarbon fields	6
Deep saline aquifers	2660
Coal seams	27
total	**2693**

In Hydrocarbon fields

The estimation of CO_2 storage capacity in Bulgarian hydrocarbon fields is based on evaluation of all discovered 12 economic fields (Fig. 10). However most of them are out of right depth interval for effective CO_2 storage, which is 800 – 2500 m. Only in two gas fields, respectively Tchiren and Galata, the depth window for the reservoirs is favorable. But Tchiren field was converted into sub-surface gas storage in 1974 and still operating.

So, only Galata gas field (located offshore) was considered for estimation of CO_2 storage capacity. Nevertheless that this field is small, it suggests good opportunities for CO_2 storage (excellent reservoir parameters and depth). However there is a big interest for conversion of this field after depletion into sub-surface gas storage.

The storage capacity of the gas fields has been estimated assuming a 1:1 volumetric replacement ratio between hydrocarbons and CO_2. The CO_2 density varies with depth as a function of pressure and temperature and has been estimated using diagrams.

In Aquifers

Aquifers or deep saline water bearing layers offer enormous CO_2 storage potential, because they usually have larger spreading and good reservoir qualities. Important requirement to them is to have effective seals, presented by no permeable geological formations.

The presence of reservoir strata, horizons and levels in sedimentary succession of main tectonic units in Bulgaria is pictured in Fig. 8. Generally speaking, in the sedimentary successions of different basins and zones (Fig. 4) dominated not-permeable and semi-permeable formations and the presence of reservoir strata, horizons or levels is usually with local or zonal spreading.

The assessment of aquifers and their potential for CO_2 storage in Bulgaria was made after detailed study and analyses of:

- the presence of appropriate lithology for good reservoirs;
- the presence of favourable seismic facieses;
- the received amount of fluid flow during the tests in the boreholes;
- the presence of negative anomaly in SP log curve;
- the mud circulation louse during the drilling (mud engulf);
- the lab analyses of reservoir parameters porosity and permeability;
- the buried depth of reservoir formations – is it effective for CO_2 storage?

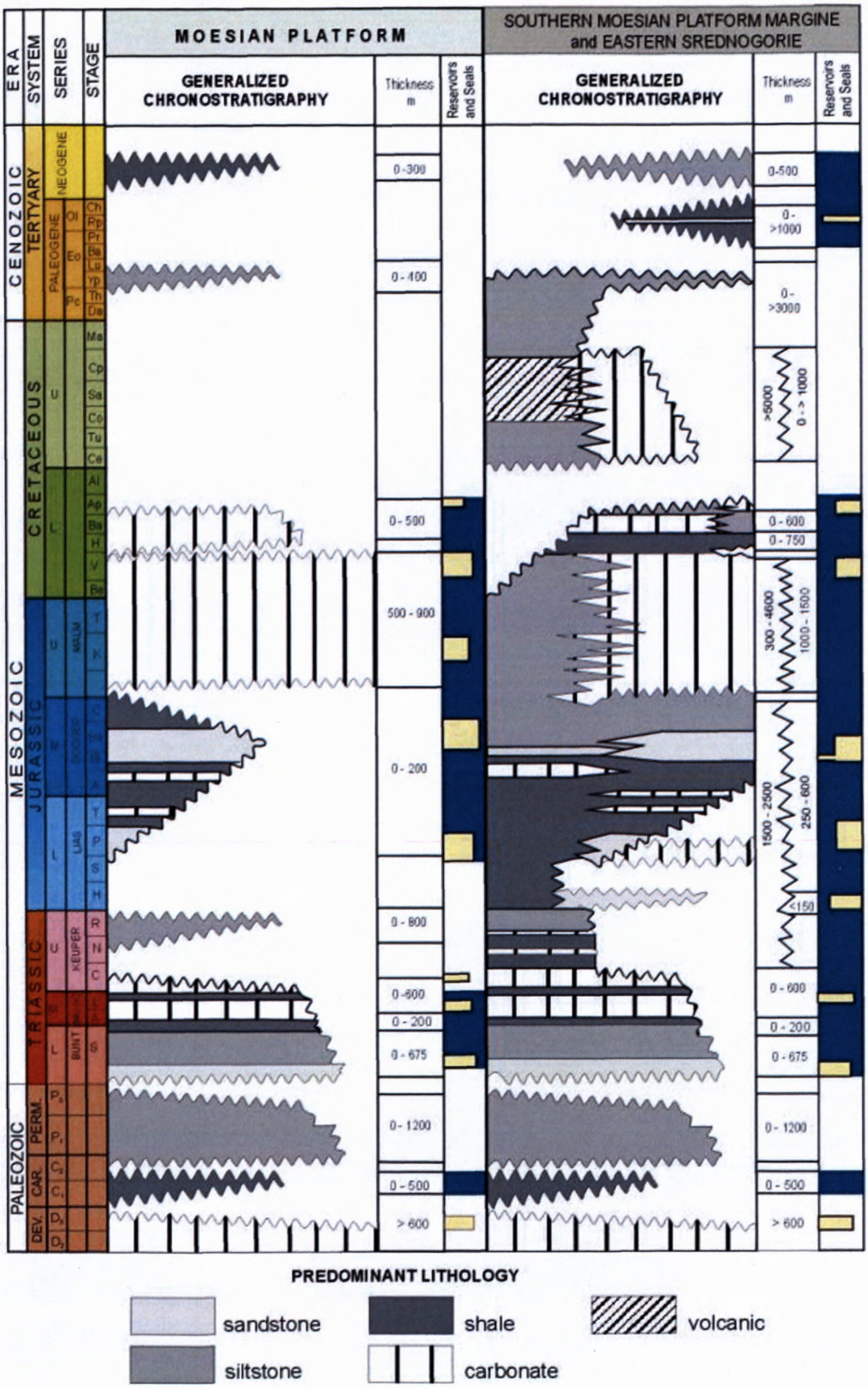


Fig. 8 A schematic Litho-Stratigraphic chart for sedimentary succession in the Moesian platform, Southern platform margin and Eastern Srednogorie-Balkan zone with reservoir / seal distribution (Georgiev & Dabovski, 2000 - improved).

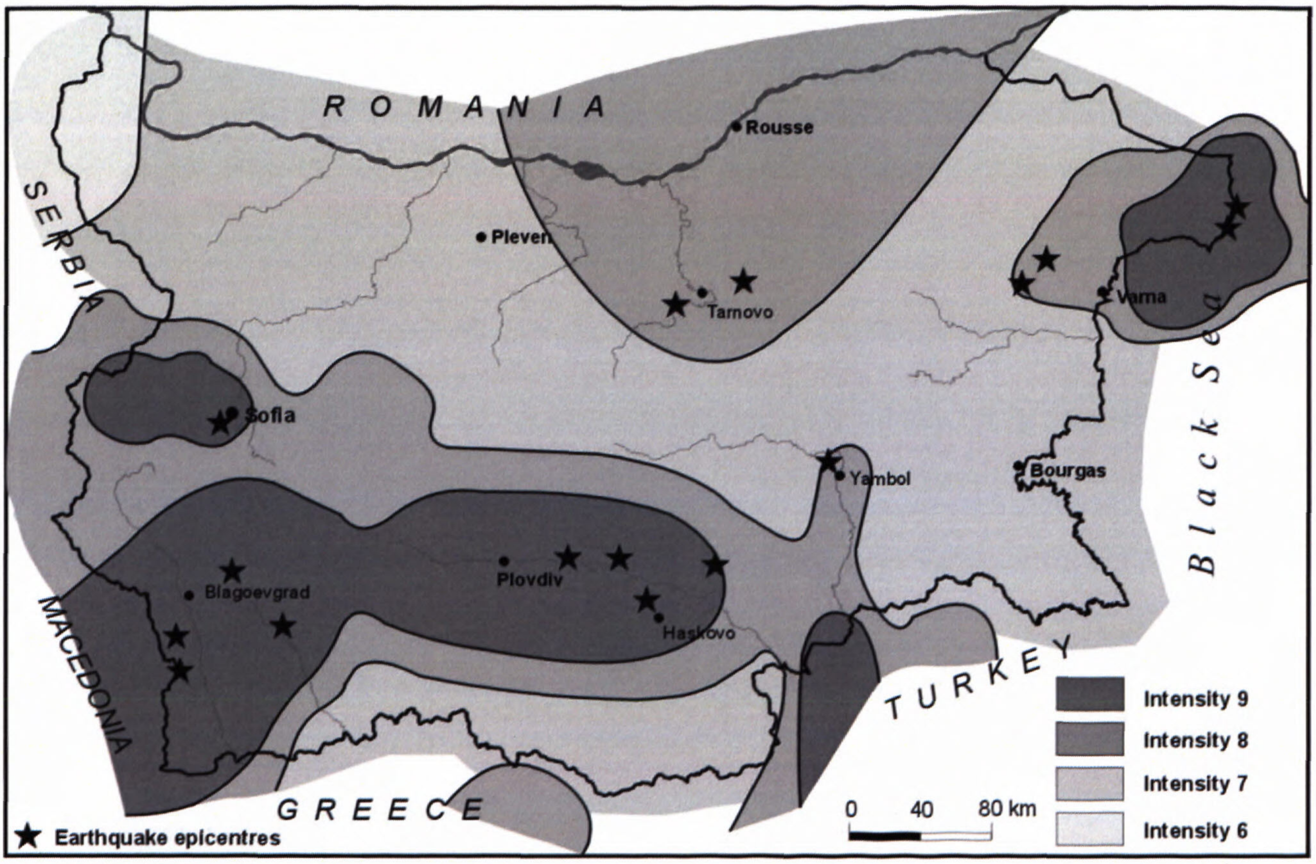
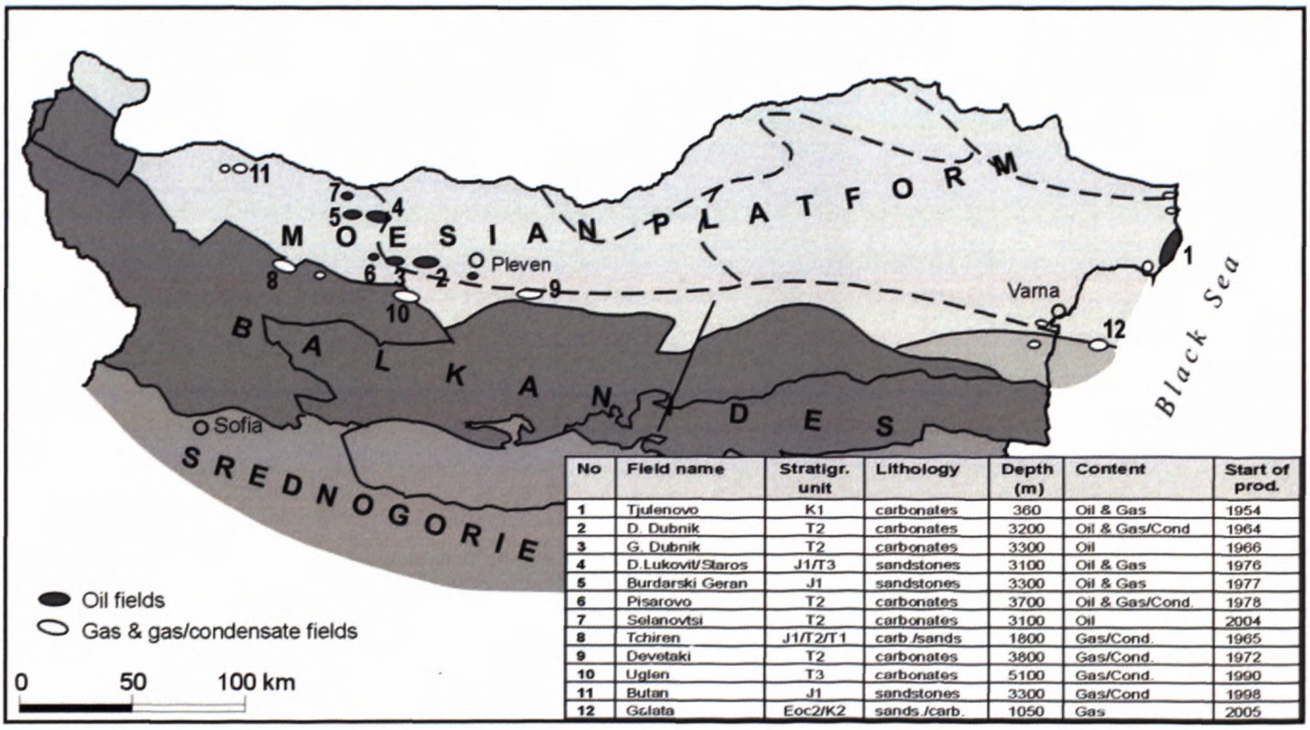


Fig. 9 Recorded stronger earthquakes and prognosis seismic intensity (by MSC-64) in Bulgaria (by Bonchev et al., 1982 – modified and updated).



No	Field name	Stratigr. unit	Lithology	Depth (m)	Content	Start of prod.
1	Tjulenovo	K1	carbonates	360	Oil & Gas	1954
2	D. Dubnik	T2	carbonates	3200	Oil & Gas/Cond	1964
3	G. Dubnik	T2	carbonates	3300	Oil	1966
4	D.Lukovit/Staros	J1/T3	sandstones	3100	Oil & Gas	1976
5	Burdarski Geran	J1	sandstones	3300	Oil & Gas	1977
6	Pisarovo	T2	carbonates	3700	Oil & Gas/Cond.	1978
7	Selanovtsi	T2	carbonates	3100	Oil	2004
8	Tchiren	J1/T2/T1	carb./sands	1800	Gas/Cond.	1965
9	Devetaki	T2	carbonates	3800	Gas/Cond.	1972
10	Uglen	T3	carbonates	5100	Gas/Cond.	1990
11	Butan	J1	sandstones	3300	Gas/Cond	1998
12	Galata	Eoc2/K2	sands./carb.	1050	Gas	2005

Fig. 10 Summary of Bulgarian economic hydrocarbon fields.

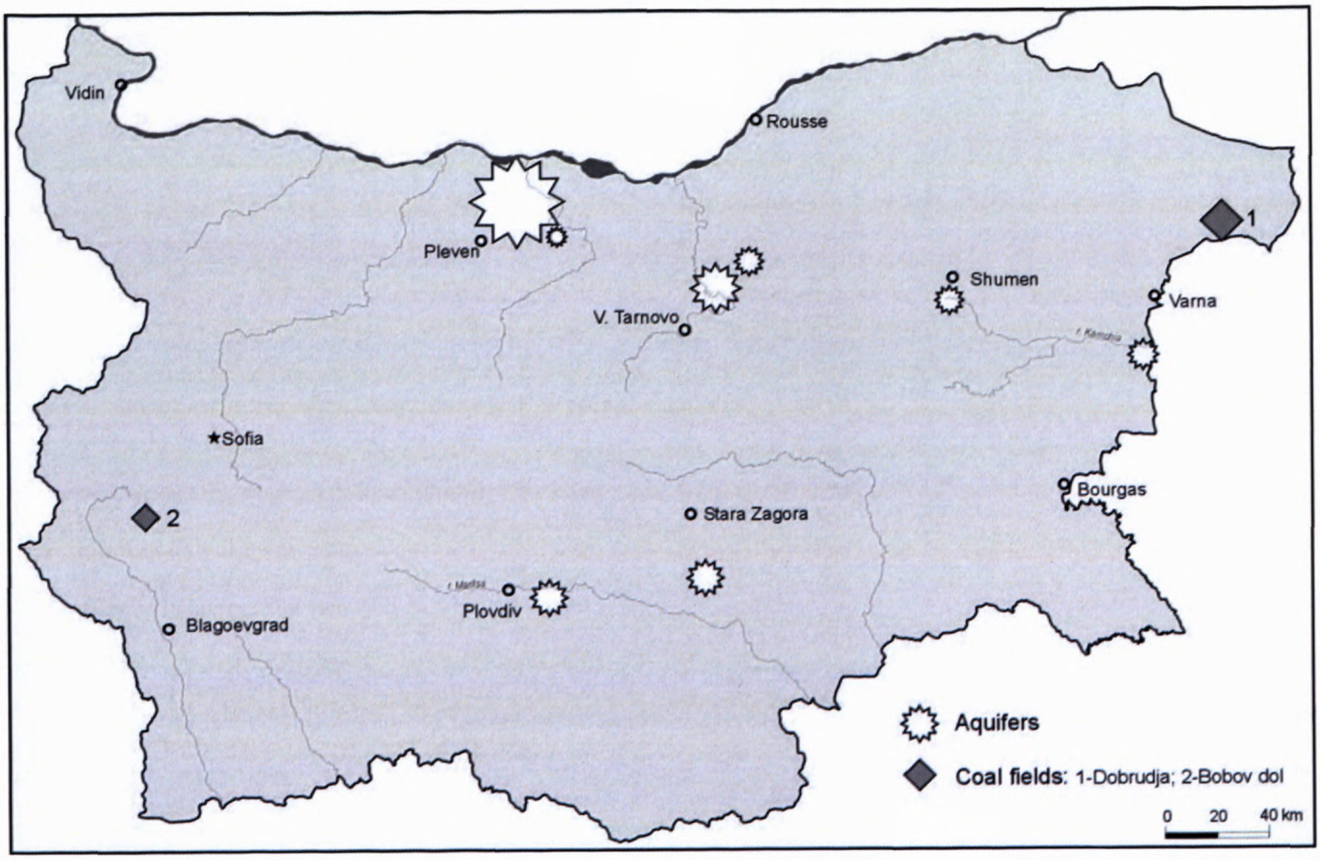


Fig. 11 Location of selected and estimated aquifers (zonal and structural) and coal fields in Bulgaria.

Volumetric storage capacity was calculated using methodology of Brook at al., 2003 and Bachu et al., 2007, accepted in EU GeoCapacity project, expressed by the formula:

$$\mathbf{M_{CO2} = A \times h_{ef} \times \phi \times \rho_{CO2} \times S_{eff}}$$

where:

M_{CO2} - storage capacity within a geological structure
A - area of aquifer
h_{ef} - effective thickness of aquifer reservoir
ϕ - reservoir porosity
ρ_{CO2} - CO_2 density at reservoir conditions
S_{eff} - storage efficiency factor

The most promising potential for CO_2 storage in Bulgaria related with some karstified and fractured carbonate reservoirs in the Devonian and Upper Jurassic – Valanginian, and some coarse-grained clastic reservoirs in the Lower Triassic, Middle Jurassic and Middle-Upper Eocene stratigraphic units (Fig. 8). All they were proved by received results from numerous drilled oil and gas exploration wells.

The evaluation of CO_2 storage capacity in deep saline aquifers in Bulgaria is based on estimation of 2 individual structures and 6 local zones, shown on Fig. 11. They related respectively with Devonian, Lower Triassic, Middle Jurassic, Upper Jurassic - Valanginian and Middle-Upper Eocene reservoirs (Fig. 8). Six of selected aquifers are located in Northern Bulgaria, other two in Southern Bulgaria.

In Coal seams

Most of un-mined coal reserves in Bulgaria occur at shallow depth, no favorable for safety injection of CO_2. Deeper occurrence of coal-bearing formations (>800 m), suitable for CO_2 storage, exists only in two fields - Dobudja and Bobov Dol (Fig. 11). In GeoCapacity project was made first evaluation of geological conditions in order to estimate CO_2 storage feasibility and capacity in coal seams within these two fields.

The CO_2 storage capacity in coal field (S) is a function of PGIP (producible gas in place), CO_2 (gas) density and CO_2 to CH_4 exchange ratio (ER) (Bergen & Wildenborg, 2002):

$$S = PGIP \times CO_2 density \times ER$$

CO_2 storage capacity ***S*** denotes quantity of CO_2 which could replace PGIP, to the extent specified by ER (hard coal has usually the ratio of about 2, brown coal and lignite may have higher ratios).

PGIP means coal bed methane reserves for CO_2-Enhanced Coal-Bed Methane Recovery with the use of CO_2 storage.

Main conclusions

The largest capacity of potential CO_2 storage options in Bulgaria related with aquifers, coal fields have considerably less opportunities, while the possibilities to use depleted hydrocarbon fields practically there are not.

The duration of the estimated CO_2 storage country capacity (Table 1) with regard to annual industrial CO_2 emissions (if they save the level from 2006 - 52.2 Mt/y), is for more than 50 years.

The main problem for the geological storage of Bulgarian industrial CO_2 emissions is that the selected and estimated country storage options are located far from major CO_2 sources. Main storage capacities related to Northern Bulgaria, where the sedimentary succession is thick several kilometers and aquifers with limited spreading (structural and zonal) are present. However, the main concentration of industrial CO_2 is mainly in Southern Bulgaria, where the storage capacities are considerably less.

Some of the selected and estimated geological CO_2 storage options, as both coal fields and aquifers near to Plovdiv and V. Tarnovo (Fig. 11) are located in zones with heightened seismicity (Fig. 9), which made them risky in some extent.

The selected and estimated geological CO_2 storage options need further investigations and qualification based on: (1) larger utilization and deeper analyses of available wells and seismic information and (2) some new seismic data and wells.

The presented estimation of geological CO_2 storage options can be characterized as a slightly conservative, because some of the used values for some calculative parameters are a little bit less than expected. So, in further development of investigations and qualification of selected options there are real opportunities for increasing of national CO_2 geological storage potential.

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Permanent disposal of CO_2 industrial emission via artificial carbonatization of metaperidotite, metawehrlite and metawebsterite: an experimental study

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Abstract. The paper extends an experimental base for possibility to store the carbon dioxide emission via artificial carbonatization of metaperidotite bodies located in the East Slovakia. Three types of hydrated mantle rocks, metaperidotite (metalherzolite), metawehrlite and metawebsterite were subjected to reaction with water and CO_2 and therefrom obtained suspensions were heated by the different temperatures of 50°C, 160 °C and 200 °C in the laboratory conditions. From the heated suspensions the acid carbonates (nesquehonite, barringtonite, dypingyte, 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 amount from 902 to 1264 kg of CO_2 can be sequestered in 1 m^3 of the source metaperidotite, metawehrlite and metawebsterite.

Key words: CO_2 disposal, artificial carbonatization, acid carbonates, carbonates, CO_2 storage capacity, metaperidotite, serpentinite

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 inside of the Earth. Nowadays it is estimated that its 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 risks and it demands an urgent global response. The methods to remove the anthropogenous carbon dioxide is a sequestration, understood as catching 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 blowing to the atmosphere, while the monitoring of CO_2 leakages from the CO_2 stored deposit has to be continuous.
- chemical – by mineral carbonation ("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 magnesian serpentinite or forsteritic olivine favors 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, dypingyte 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 forms 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 on the surface in conformity with reactions 1, 2, and 3 (Johannes, 1968; Martin & Fyfe, 1970, Malakhov, 1971):

$$\underset{\text{olivine}}{2Mg_2SiO_4} + 3H_2O = \underset{\text{chrysotile}}{Mg_3Si_2O_5(OH)_4} + \underset{\text{brucite}}{Mg(OH)_2} \qquad (1)$$

$$\underset{\text{olivine}}{(Mg,Fe,Ni)_2SiO_4} + nH_2O = \text{serpentine group} + \text{magnetite}$$

$$+ MgO + H_2 \qquad (2)$$

$$\underset{\text{olivine}}{Mg_2SiO_4} + \underset{\text{enstatite}}{MgSiO_3} + 2H_2O = \underset{\text{chrysotile}}{Mg_3Si_2O_5(OH)_4} \qquad (3)$$

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:

$$(4)$$

$$\underset{\text{chrysotile}}{Mg_3Si_2O_5(OH)_4} + 3CO_2 \xrightarrow[150^{\circ}C\ +\ 150\ \text{atm}\ CO_2]{1M\ NaCl\ +\ 0.64M\ NaHCO_3} \underset{\text{magnesite}}{3MgCO_3} + SiO_2 + H_2O$$

$$\underset{\text{brucite}}{Mg(OH)_2} + CO_2 = \underset{\text{magnesite}}{MgCO_3} \qquad (5)$$

In term of reaction 4 is deducible, that for sequestration of 1 tone of CO_2 is necessary to utilize rock weight from 2.1 to 3.18 tons 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 its 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 on localities 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 by variable content of carbonate finds (Hovorka et al., 1985). It means that their evaluation for account of carbon dioxide sequestration requests detailed mineralogical and petrological study. However this is not the only criteria for usable serpertinite body, but its volume, depth, morphology and tectonic structure are important too.

A dominant CO_2 producer in Slovakia is US STEEL Ltd. with annual production more than 11 Mtons per year. Due to fact, that surrounding of this plant from geological point of view are suitable for CO_2 storage by various methods. The area near the producer is aimed at the largest ultramafic body of metaperidotite, with extension about several km^3. The outcrop of metaperidotite is located near Hodkovce. In addition besides of the Komárovce – Hodkovce large body, there is located small metawebsterite body near Rudník and the metawehrlite body near Jasov, both have 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 metaperidoite body because the reactions 4 and 5 which transform serpentinite to carbonates have an optimum temperature interval from 70 to 130 °C. Such a temperature 59 °C 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 test of 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).

2. Mineral composition of source mantle rocks

The serpentinized mantle-derived rocks were studied at localities Hodkovce (HO-1 and HO-2, metaperidotite), Rudník (RU-1 and RU-2, metawebsterite) and Jasov (JA-1 metawehrlite). The minerals of serpentine group are prevailing over the former magmatic mineral association (olivine and pyroxenes). Therefore it is possible to classify all studied rocks 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 %). The content of Cr-spinel is in the both samples less than 0.5 %. Moreover, it is possible to recognize hornblende, hornblende – pargasite, tremolite, Ni sulphides and talc in accessory quantity.

Metawebsterite is formed by antigorite + chrysotile (68 vol. %, or 77 %), Al-enstatite + Al-dioside ± fayalite (20 %, or 13 %), magnetite prevails over oxide mineral association: pyrophanite + Mn-rutile + Cr-magnetite (together 5 %); calcite (7.9 % or 3.6 %). Content of Al-spinel in both samples is below 0.5 %. Following minerals can be found in accessory concentrations: pargasite + millerite + Si-mineral (quartz?) + melanite + Cr-garnet + schwaningite + chlorite + cronstedtite – kellyite + Ba-asbolane (?) + Co-Mn mineral (?) + andratite + diabanite and barite.

Metawehrlite is composed of lizardite + chrysotile + antigorite + Ni-Fe serpentine (79 vol. %). Ti-diopside + Na-diopside + diopside ± olivine (8 %); magnetite + Cr-magnetite + hematite + Cr-hematite + Mn-hematite (together 7 %) dominates over oxide and carbonate association: rutile + calcite + Cr-spinel (6 %). This rock sporadically contains millerite + siegenite + melanite + grosular + andratite + ernienickelite + Cr-chlorite.

3. Sample preparation and analytical conditions

Polished thin sections of source metaperidotite, metawehrlite and metawebsterite were studied under polarizing microscope. We have focused on 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 at State Geological Institute of Dionýz Štúr, Bratislava. 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-wolastonite, 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 at State Geological Institute of Dionýz Štúr, Košice and silicate analyses were obtained by differential termogravity analyses (Tuček et al., 2009).

Experimental study has been conducted at such dressed samples. Serpentinite was mixed with water and carbon dioxide according to the procedure used by Tuček et al., (2009). Stable temperature, 22 °C and CO_2 pressure from 0.1 to 0.3 MPa was maintained during controlled reaction from 5 to 20 hours. Leaches, with pH value about 8 become 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 the optical methods and were analysed and controlled by electron microprobe, by CHA (chemical silicate analyses) RTG (X-ray diffraction analyses), by DTA (differential thermic analyses) and by DTG (differential thermo-gravimetric analyses) where the almost end-member of acid carbonates and carbonates have been found.

The photos of artificial carbonatization products have been 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 analyses.

4. 1 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 upraised from the suspension (serpentinite + CO_2 + H_2O) after reaction, filtration and crystallization from the filtrate (Fig. 2). Original source rock - metaperidotite was during experiment under constant temperature of 50 °C. A mixture of radial or omnidirectional aligned nesquehonite was formed from the original metawehrlite. The nesquehonite is sporadically fibrillated by a hemisphere of dypingite, and hydromagnesite (Fig. 4). The original calcite, which was formed in metawehrlite during its serpentinisation, was in time nesquehonite and dypingyte formation hydrated, while original dolomite remained stable without its chemical composition changes (Fig. 4d).

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 $K_{0.001}Ca_{0.001}Mg_{0.999}CO_3.2H_2O$; dypingite $K_{0.003}\,Na_{.0.008}\,Si_{0.061}\,Al_{0.016}\,Fe_{0.03}\,Cr_{0.053}\,Ca_{0.090}\,Mg_{4.765})_5(CO_3)_4(OH)_2.5H_2O$ 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. 5, Tab. 2).

In hydromagnesite and dypingite the Cr_2O_3 content ranges from 0.41 wt. % to 1.42 % and the highest content of Cr_2O_3 in nesquehonite reaches 0.11 % (Fig. 12). The variable content of Cr_2O_3 indicates a bond of Cr as the stichtite molecule in hydromagnesite and dypingite.

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 (Fig. 5). 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. 1). Low element contents were omitted in chemical formulas.

(metaperidotit source)

$$\underset{\text{serpentine group}}{Mg_3Si_2O_5(OH)_4} + 3CO_2 + 6\,H_2O \xrightarrow{50^\circ C\,+\,0.1MPa\ CO_2} \underset{\text{nesquehonite}}{2MgCO_3.3H_2O} + \underset{\text{barringtonite}}{MgCO_3.2H_2O} + SiO_2 \qquad (6)$$

The coexisting mixture of nesquehonite and hydromagnesite was formed after the reaction of chrysotile with water and carbon dioxide. The mixture of acid carbonates formed from the metawehrlite-matrix was in conformity with reaction 7 by the same temperature of 50 °C (Fig. 5). The set up and procedure of the reaction 7 was identical as in the previous case (6).

(metawehrlite sourse)

$$\underset{\text{serpentine group}}{2Mg_3Si_2O_5(OH)_4} + 5CO_2 + 4H_2O \xrightarrow{50^\circ C\,+\,0.1MPa\ CO_2} \underset{\text{nesquehonite}}{MgCO_3.3H_2O} + \underset{\text{hydromagnesite}}{Mg_5(CO_3)_4(OH)_2.4H_2O} + 2SiO_2 \qquad (7)$$

The formation of two different coexisting pairs, nesquehonite – barringtonite and nesquehonite – hydromagnesite were formed at the same temperature 50 °C on the expense of chrysotile after reactions 6 and 7. Two different pairs are possible to clarify by different reaction activity in the source metaperidotite and metawehrlite from which the chrysotile was formed. Olivine, enstatite and diopside replaced by chrysotile during metamorphism or hydration of peridotite have probably different reaction ability (activity) than from the chemical point of view identical to chrysotile which was formed in metawehrlite by the hydration of diopside. In conformity with juxtaposition of reactions 6 and 7, metawehrlite consumes less amount of CO_2 during artificial carbonatization than metaperidotite.

Tab. 1 Representative analyses of acid carbonates formed during artificial carbonatization by temperature 50 °C. Neq-nesquehonite, Bar-barringtonite, Dyp-dypingite, hMag-hydromagnesite.

Sample Mineral Rock Temper.	HO-1 Neq peridotite 50 °C	HO-1 CaNeq peridotite 50 °C	HO-2 Neq peridotite 50 °C	HO-1 Bar peridotite 50 °C	HO-2 Bar peridotite 50 °C	JA-1 Neq wehrlite 50 °C	JA-1 Neq wehrlite 50 °C	JA-1 Dyp wehrlite 50 °C	JA-1 hMag wehrlite 50 °C
SiO_2	0.06	0.29	0.09	0	0.02	0	0	0.82	1.26
TiO_2	0	0	0	0	0	0	0	0	0
Al_2O_3	0	0.09	0	0	0	0	0.05	0	0.13
Cr_2O_3	0.06	0.08	0.03	0	0	0.11	0	0.54	0.41
FeO	0	0.03	0.07	0	0.02	0.60	0	0.02	0.08
MnO	0	0	0.02	0	0.01	0	0	0.03	0.02
MgO	28.33	17.63	29.59	32.48	32.18	27.40	29.80	35.33	40.69
CaO	0.03	17.11	0.04	0.04	0	0.09	0.05	0.56	0.99
Na_2O	0	0.06	0	0	0.04	0	0	0.09	0.02
K_2O	0	0.01	0	0.04	0	0	0.02	0.03	0.03
Cl	0	0.08	0	0	0	0	0.02	0.61	0.84
H_2O*	38.20	40.67	39.98	29.08	28.83	37.40	40.10	19.27	18.38
Total	66.69	76.05	69.82	61.64	61.10	65.60	70.04	57.30	62.85
CO_2*	33.31	23.95	30.18	38.36	38.90	34.40	29.96	42.70	37.15
Total *	100	100	100	100	100	100	100	100	100
O	4	4	4	3	3	4	4	11	10
Si	0.001	0.006	0.002	0	0	0	0	0.075	0.099
Al	0	0.002	0	0	0	0	0.001	0	0.012
Ti	0	0	0	0	0	0	0	0	0
Cr	0.001	0.001	0.001	0	0	0.002	0	0.039	0.025
Fe	0	0.001	0.001	0	0	0.012	0	0.002	0.005
Mg	0.995	0.580	0.992	0.999	0.998	0.982	0.997	4.808	4.772
Mn	0	0	0	0	0	0.002	0	0.002	0.001
Ca	0.001	0.405	0.001	0.001	0	0	0.001	0.055	0.083
Na	0	0.001	0	0	0.002	0	0	0.016	0.003
K	0	0	0	0.001	0	0	0.001	0.003	0.003
Total	0.998	0.998	0.997	1.001	1.000	0.998	1.000	5.000	5.003
CCl	0	0.006	0	0	0	0	0.002	0.189	0.224
OH	6	5.987	6	4	4	6	5.999	11.736	9.648

* calculated from chemical formula, CO_2 = 100 – Total *

4.2 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 has been formed and locally the size of crystals reach nearly 100 µm (Fig. 5). Original grains of Ca–Mg silicate (chrysotile, enstatite, diopside) were replaced by the mixture of dypingite, magnesite and dolomite. During the process of carbonatization the rare and allotriomorphic grains of dolomite and magnesite were formed reaching the size of 7 µm (Fig. 5c). Original diopside was in the course of carbonatization hydrated and replaced by hydromagnesite. (Fig. 5d)

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. 6., Tab. 3 and 4). In hydromagnesite the Cr_2O_3 content ranges from 0.11 wt. % to 1.85 % and in dypingite ranges 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 was formed the acid carbonates as well. The Cr_2O_3 content was not determined in magnesite, dolomite and calcite (Fig. 11).

The new assemblage of hydromagnesite, magnesite, dolomite and calcite is the final product of reaction 8 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 3 and 4). The small content of elements was neglected in the chemical formula.

(metaperidotite source)

$$\underbrace{Mg_3SiO_2(OH)_4}_{\text{serpentine group}} + \underbrace{CaMgSi_2O_6}_{\text{diopside}} + \underbrace{Mg_2SiO_4}_{\text{olivine}} + 6CO_2 + 3H_2O \xrightarrow{160\,^{\circ}C \text{ and } 200\,^{\circ}C + 0.1MPa\ CO_2} \underbrace{Mg_5(CO_3)_4(OH)_2.4H_2O}_{\text{hydromagnesite}} + \underbrace{MgCO_3}_{\text{magnesite}} + \underbrace{CaCO_3}_{\text{calcite}} + 5SiO_2 \qquad (8)$$

Tab. 2 Representative analyses of acid carbonates formed during artificial carbonatization by temperature 160 and 200 °C. Neq-nesquehonite, Bar-barringtonite, Dyp-dypingite, Ser- sergeevite, hMag-hydromagnezit.

Sample	HO-2	HO-2	HO-2	HO-1	HO-2	HO-2	HO-2	HO-2	RU-1	RU-1	RU-1	RU-1	RU-1	RU-1
Mineral	Dyp	hMag	hMag	Dyp	Ser	hMag	Neq	Bar	Dyp	Ser	hMag	hMag	Neq	Bar
Rock	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite	peridotite	webste.	webste.	webste.	webste.	webste.	webste.
Temper.	160°C	160°C	160°C	200°C	200°C	200°C	200°C	200°C	200°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	0.05	2.03	0.65	0.91	0.48	0.83
TiO_2	0	0	0	0	0	0	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	0	0.01	0	0	0	0.01
Cr_2O_3	1.02	1.80	0.11	0.13	0.02	0.18	0.10	0.03	0.10	0.14	0.16	4.16	0.78	0.09
FeO	0.03	0	0.05	0.03	0.34	0.06	0.01	0	0	0.03	0	0	0	0
MnO	0.06	0.03	0.07	0.01	0	0	0	0	0.03	0.02	0	0.04	0.02	0.01
MgO	38.57	43.14	41.36	34.54	20.19	43.28	28.16	34.73	39.40	31.63	40.41	37.64	29.20	23.38
CaO	0.57	0.76	0.48	1.39	19.27	0.61	0.39	0.53	0.37	7.63	1.22	0.63	0.35	7.98
Na_2O	0.10	0.16	0.02	0.04	0.01	0.02	0.02	0.04	0.26	0.03	0.09	0.04	0.21	0
K_2O	0.06	0.10	0.02	0.01	0	0	0.01	0.02	0.02	0.02	0.07	0.03	0.06	0.01
Cl	0.10	0.27	0.26	0.05	0.13	0.26	0.11	0.10	0.16	0.04	0.08	0.58	0.55	0.03
H_2O*	21.22	19.89	18.67	19.23	11.73	19.46	38.51	31.60	21.54	12.66	18.55	17.43	40.48	26.34
Total	61.98	67.11	62.01	57.07	52.05	64.77	67.89	67.70	61.93	54.25	61.23	61.46	72.14	58.68
CO_2*	38.02	32.89	37.99	42.93	47.05	35.23	32.11	32.30	38.07	45.75	38.77	38.54	27.86	41.32
Total *	100	100	100	100	100	100	100	100	100	100	100	100	100	100
O	11	10	10	11	23	10	4	3	11	23	10	10	4	3
Si	0.021	0.07	0.076	0.149	0.086	0.066	0.013	0.012	0.004	0.458	0.052	0.074	0.011	0.019
Al	0	0.01	0	0.001	0.006	0.002	0.001	0	0	0.003	0	0	0	0
Ti	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Cr	0.068	0.105	0.007	0.009	0.004	0.011	0.002	0	0.007	0.025	0.010	0.29	0.014	0.002
Fe	0.002	0	0.003	0.002	0.072	0.004	0	0	0	0.006	0	0	0	0
Mg	4.832	4.729	4.861	4.694	7.607	4.874	0.975	0.976	4.909	10.642	4.816	4.590	0.959	0.786
Mn	0.004	0.002	0.005	0.001	0	0	0	0	0.002	0.006	0	0.003	0	0
Ca	0.051	0.060	0.041	0.136	5.218	0.049	0.010	0.011	0.033	1.845	0.104	0.055	0.008	0.193
Na	0.016	0.023	0.003	0.007	0	0.003	0.001	0.001	0.042	0.013	0.014	0.006	0.009	0
K	0.006	0.009	0.002	0.001	0.003	0	0	0	0.002	0.006	0.007	0.003	0.002	0
Total	5.000	4.999	4.998	5.000	12.996	5.009	1.002	1.000	4.999	13.004	5.003	5.000	1.003	1.000
CCl	0.028	0.067	0.070	0.015	0.111	0.067	0.009	0.006	0.045	0.031	0.022	0.161	0.041	0.002
OH	11.896	9.756	9.815	11.692	19.774	9.807	5.966	3.972	12.007	19.055	9.889	9.510	5.949	3.961

* calculated from chemical formula CO_2 * = 100 – Total *

Tab. 3 Representative analyses of carbonates formed during artificial carbonatization. Cal-kalcite, Dol-dolomite, Mag-magnesite.

Sample	Ja-1	HO-2	HO-2	HO-2	HO-2	HO-2	RU-2	HO-2	HO-2	HO-2
Mineral	Dol-relikt	Cal	Dol	CaMag	Mag	Cal	Cal	Dol	CaMag	Mag
Rock	wehrlite	peridotite	peridotite	peridotite	peridotite	peridotite	websterite	peridotite	peridotite	peridotite
Temper.	50 °C	160 °C	160 °C	160 °C	160 °C	200 °C	200 °C	200°C	200 °C	200 °C
FeO	0.88	0	0	0.02	0	0	0.01	0.04	0	0
MnO	0.05	0.03	0	0	0.03	0.11	0.02	0	0.01	0.10
MgO	25.23	0.85	27.03	39.42	46.70	1.40	1.72	27.58	40.73	47.59
CaO	25.93	55.45	24.12	10.08	0.87	54.49	53.76	23.10	7.34	0.28
CO_2^*	48.46	44.45	48.46	50.96	51.69	44.36	44.10	48.28	50.26	52.24
Total	100.55	100.78	99.61	100.48	99.29	100.36	99.61	99.00	98.34	100.21
O	6	3	6	3	3	3	3	6	3	3
Fe	0.022	0	0	0	0	0	0	0.002	0	0
Mn	0.002	0	0	0	0	0.002	0	0	0	0.001
Mg	1.138	0.021	1.218	0.845	0.987	0.034	0.043	1.248	0.885	0.995
Ca	0.840	0.979	0.782	0.155	0.013	0.964	0.957	0.750	0.115	0.004
Total	2.002	1.000	2.000	1.000	1.000	1.000	1.000	2.000	1.000	1.000

* calculated from chemical formula.

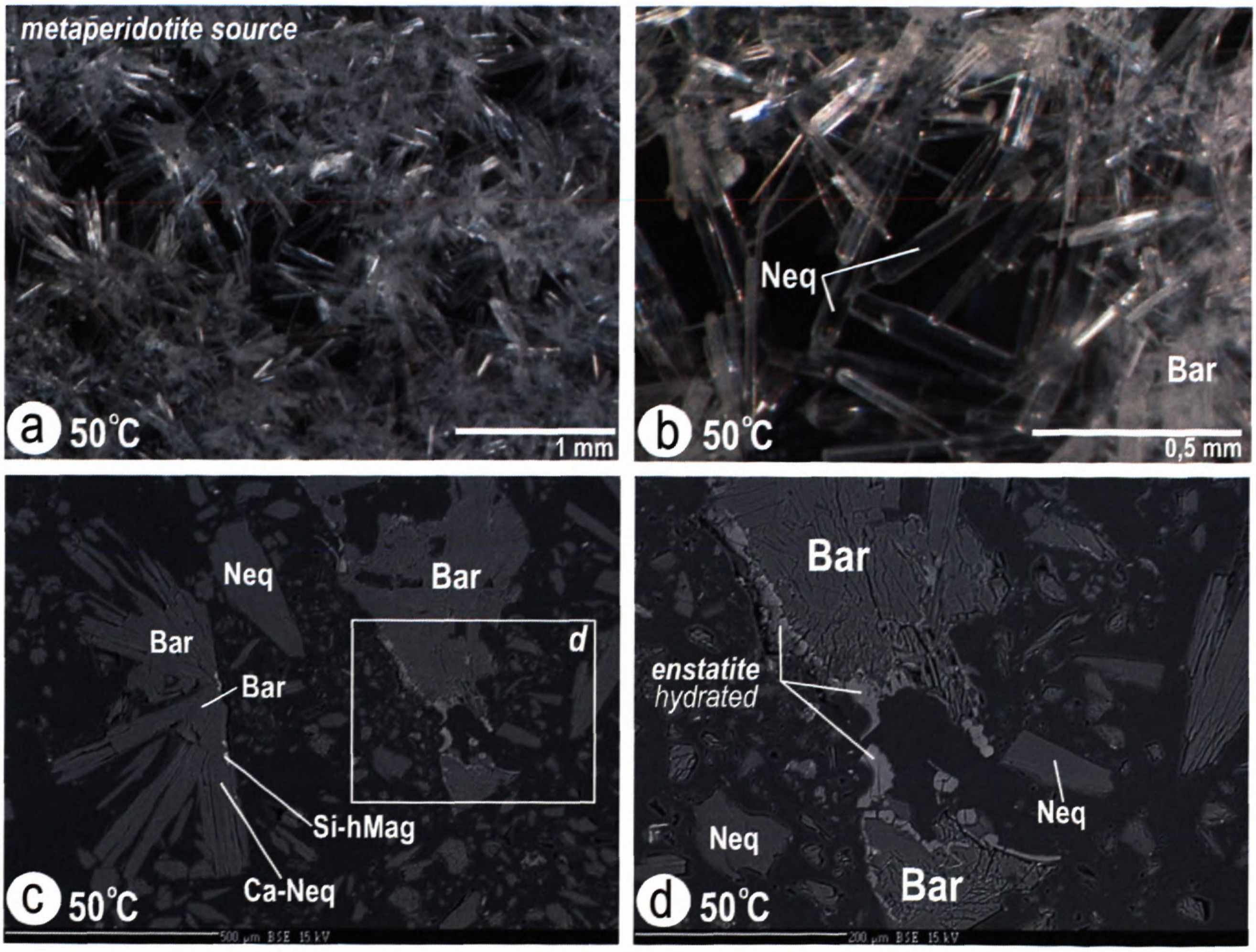

Fig. 1 Nesquehonite (Neq) and barringtonite (Bar) were formed during artificial carbonatization process at temperature 50 °C from the metaperidotite – serpentinite source. Sample HO-1., a) idiomorphic crystals of nesquehonite in binocular loupe, b) idiomorphic crystals of nesquehonite and barringtonite 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 relict hydrated enstatite and new barringtonite and nesquehonite. Back-scattered electron image.

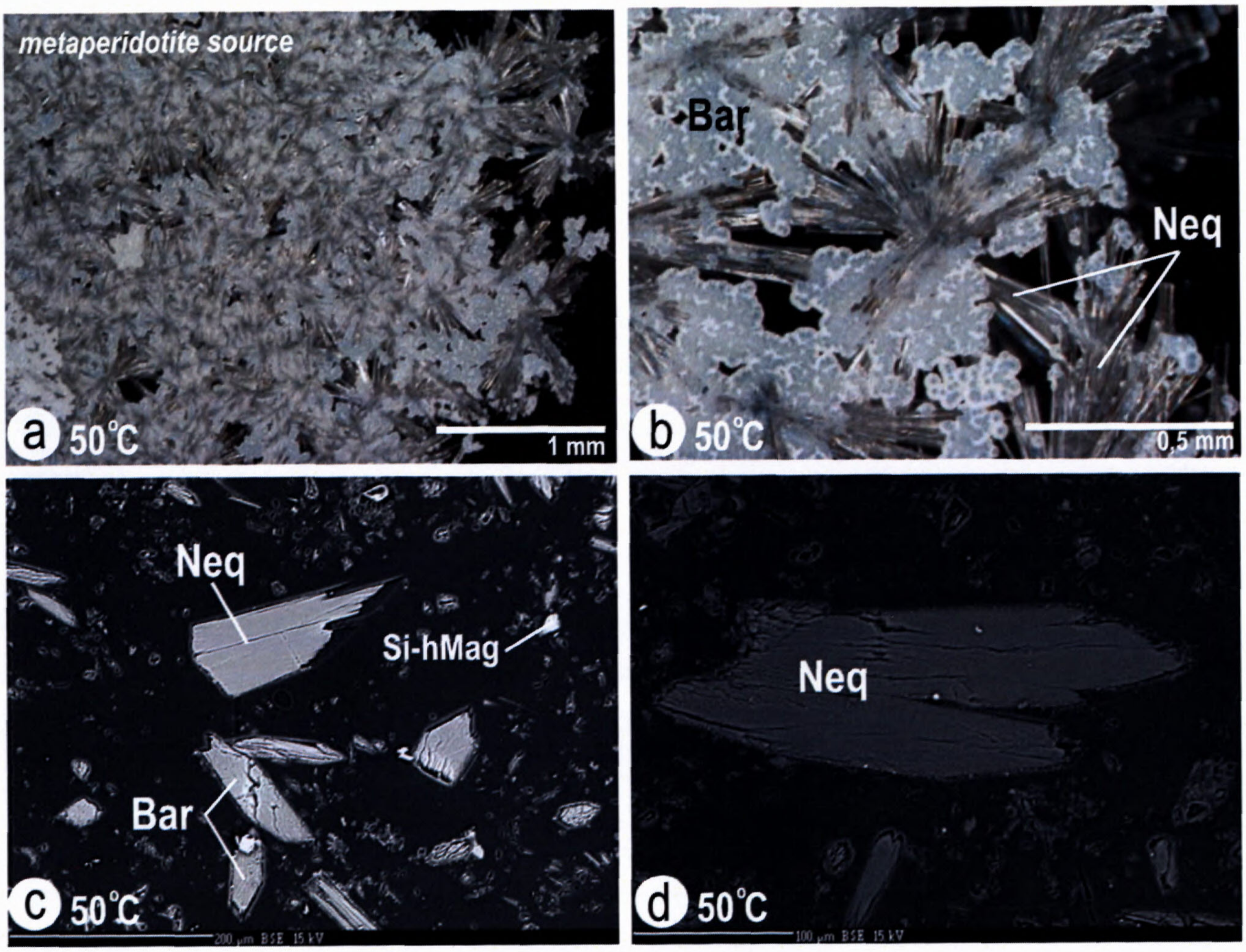

Fig. 2 Nesquehonite, (Neq), barringtonite (Bar) and hydromagnesite (hMag) formed the artificial carbonatization process at temperature 50 °C from the metaperidotite – serpentinite source. Sample HO-2., a) nesquehonite and barringtonite in binocular loupe, b) nesquehonite and barringtonite in binocular loupe; c) nesquehonite, barringtonite, Ca and Si hydromagnesite (Si-hMag). Back-scattered electron inage, d) nesquehonite in back-scattered electron image.

4.3 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 according to reaction 8 from the source metaperidotite (Figs. 7 and 8d). The spherical grains are zoned. The core forms hydromagnesite, dypingite and/or sergeevite and the rim parts of rounded grains are formed by nesquehonite and barringtonite (Figs. 7c and 7e).

A new assemblage of Si nesquehonite, nesquehonite, hydromagnesite, dypingite and calcite crystallized from the source metawebsterite. The spherical form has sergeevite and barringtonite (Fig. 8).

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. 9 and 10, Tables 3 and 4). In nesquehonite and hydromagnesite the Cr_2O_3 content is ranging from 0.79 wt. % to 2.16 % with the sporadic value of 4.16 % (Fig. 11). In this acid carbonates, the Cr_2O_3 content indicate the bond of Cr in the stichtite molecule.

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 and 8d). The same assemblage is the result of serpentine group and olivine reaction with the water and carbon dioxide which was formed by the temperature 160 °C according to the reaction 8.

Hydromagnesite, nesquehonite and calcite crystallized during the metawebsterite carbonatization where the

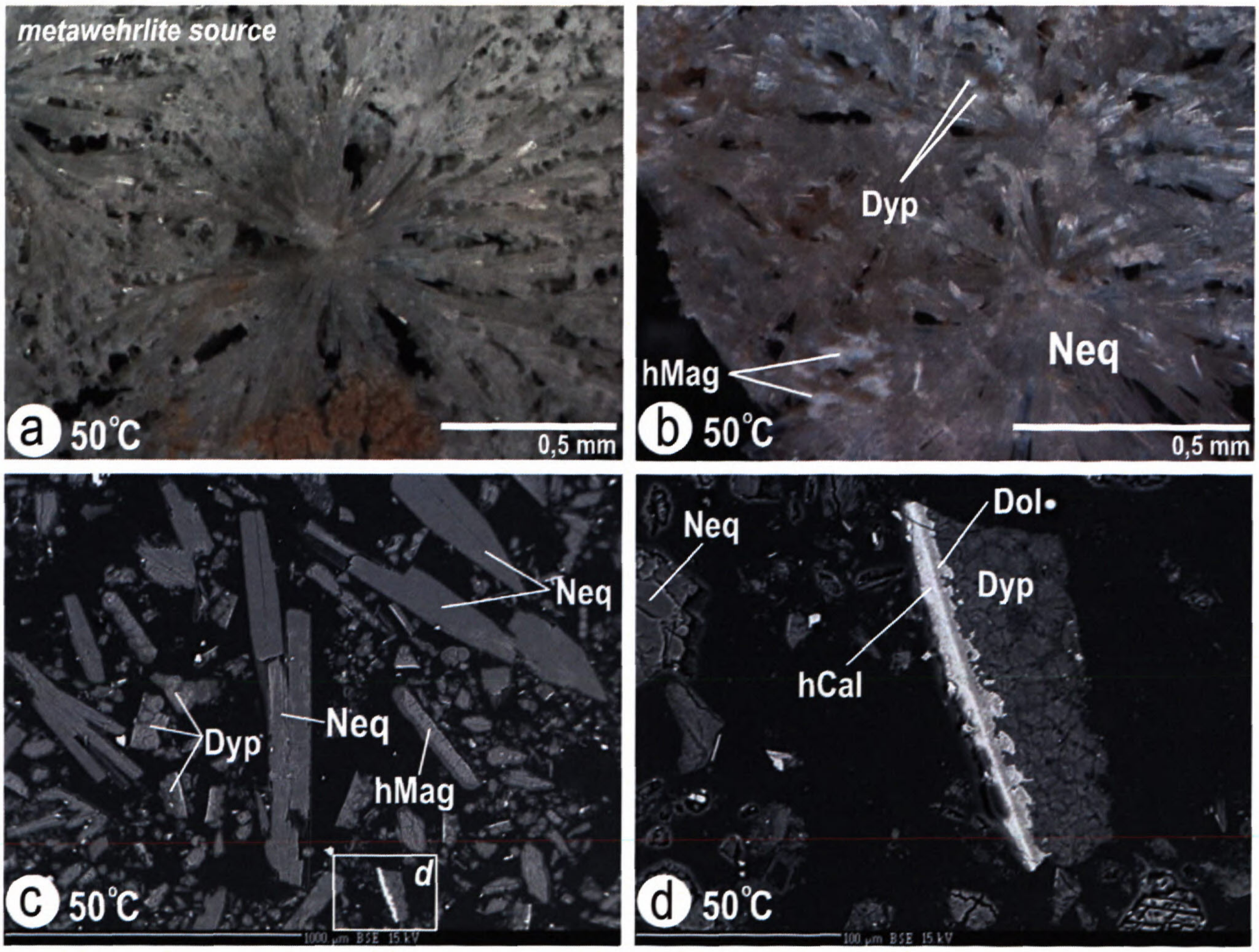

Fig. 3 Nesquehonite (Neq) and dypingite (Dyp) were formed during artificial carbonatization process at temperature 50 °C from the metawehrlite – serpentinite source. Sample JA-1., a) radial nesquehonite and dypingite in binocular loupe, b) nesquehonite and dypingite in binocular loupe, c) nesquehonite, dypingite and hydromagnesite (hMag). Back-scattered electron image., d) detail-c relict of hydrated calcite (hCal) and dolomite (Dol) replaced by dypingite and nesquehonite in back-scattered electron image.

Fig. 4 Variation of H_2O and CO_2 in coexisting pair of nesquehonite – barringtonite (sample HO-1 and HO-2 metaperidotite source) and in coexisting pair nesquehonite – dypingite/hydromagnesite (sample JA-1 metawehrlite source). These acid carbonates crystallized 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. Grey rhomb – Carbonate relics from original metawehrlite.

temperature was 200 °C (Fig. 8). The carbonatization is result of the relation between main responsive minerals in metawebsterite to new formed minerals. It is driven by cations and anions balance in chemical formulas of minerals following reaction 9 (Tables 2 and 3). The small content of elements was omitted in the chemical formula.

(metawebsterite source)

$$\underset{\text{serpentine group}}{Mg_3Si_2O_5(OH)_4} + \underset{\text{diopside}}{CaMgSi_2O_6} + \underset{\text{enstatite}}{Mg_2Si_2O_6} + 6CO_2 +$$

$$+ 6H_2O \xrightarrow{200\ ^\circ C + 0.1 MPa\ CO_2} \underset{\text{hydromagnesite}}{Mg_5(CO_3)_4(OH)_2.4H_2O} + \underset{\text{nesquehonite}}{MgCO_3.3H_2O} +$$

$$+ \underset{\text{calcite}}{CaCO_3} + 6SiO_2 \qquad (9)$$

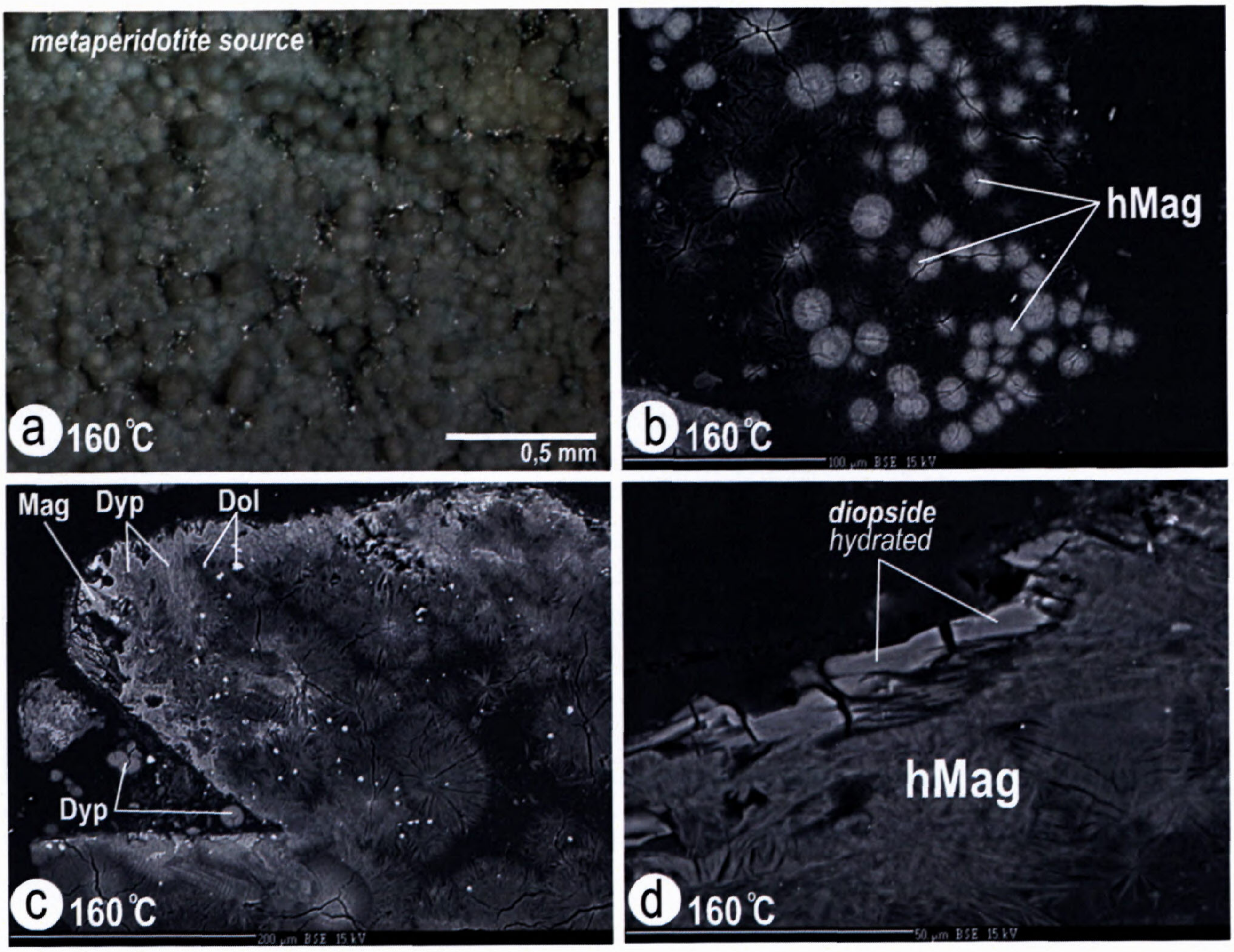

Fig. 5 Products of the artificial carbonatization were formed at temperature 160 °C from the metaperidotite – serpentinite source. Sample HO – 2 a) hydromagnesite (hMag) in binocular loupe, b) hydromagnesite in back-scattered electron image, c) The relict of enstatite replaced by magnesite (Mag), dypingite (Dyp) and dolomite (Dol). Back-scattered electron image., d) relic of hydrated diopside replaced by hydromagnesite. Back-scattered electron image.

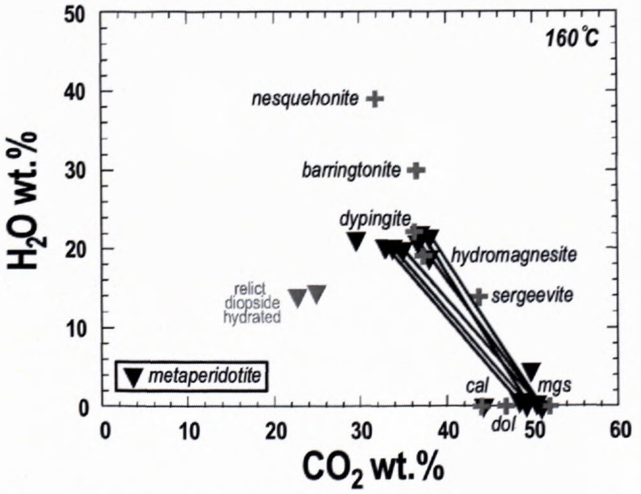

Fig. 6 Variation of H_2O and CO_2 in coexisting dypindite, hydromagnesite, calcite, dolomite and magnesite. Sample HO-2. These minerals were formed during artificial carbonatization at temperature 160 °C from the metaperidotite source. Grey plus – contents of H_2O and CO_2 in end member minerals: cal – calcite, dol - dolomite, mag – magnesite. Grey reverse triangle – content of H_2O and CO_2 in hydrated relic of diopside.

5. Discussion

The reactions 6 - 9 have been evaluated by mass balance calculations based on the relation between the source rocks of mantle and theirs respondent minerals (serpentine group, olivine, enstatite, diopside) and CO_2 + H_2O composition as well as according to new formed acid carbonates and carbonates. These reactions represent the artificial carbonation process, which can take place under various temperature conditions. A weight of carbon dioxide (kg) was calculated after the mass balance of these reactions. Consequently, it allows to asses the weight of CO_2 consumed in 1 m^3 of metaperidotite, metawehrlite or in metawebsterite during artificial carbonatization process. In the course of reaction 6 controlled by temperature 50 °C is possible to consume 1 264 kg of CO_2 in 1 m^3 of metaperidotite, if the volume density of metaperidotite is 3.0 kg/m^3. The capability of rock decreases to 1 083 kg of sequestered CO_2 in case of lower volume density 2.57 kg/m^3 that is the value typical for serpentinite.

In terms of reaction 7, when the temperature level is kept at the value 50°C, 1 m^3 of metawehrlite can elimi-

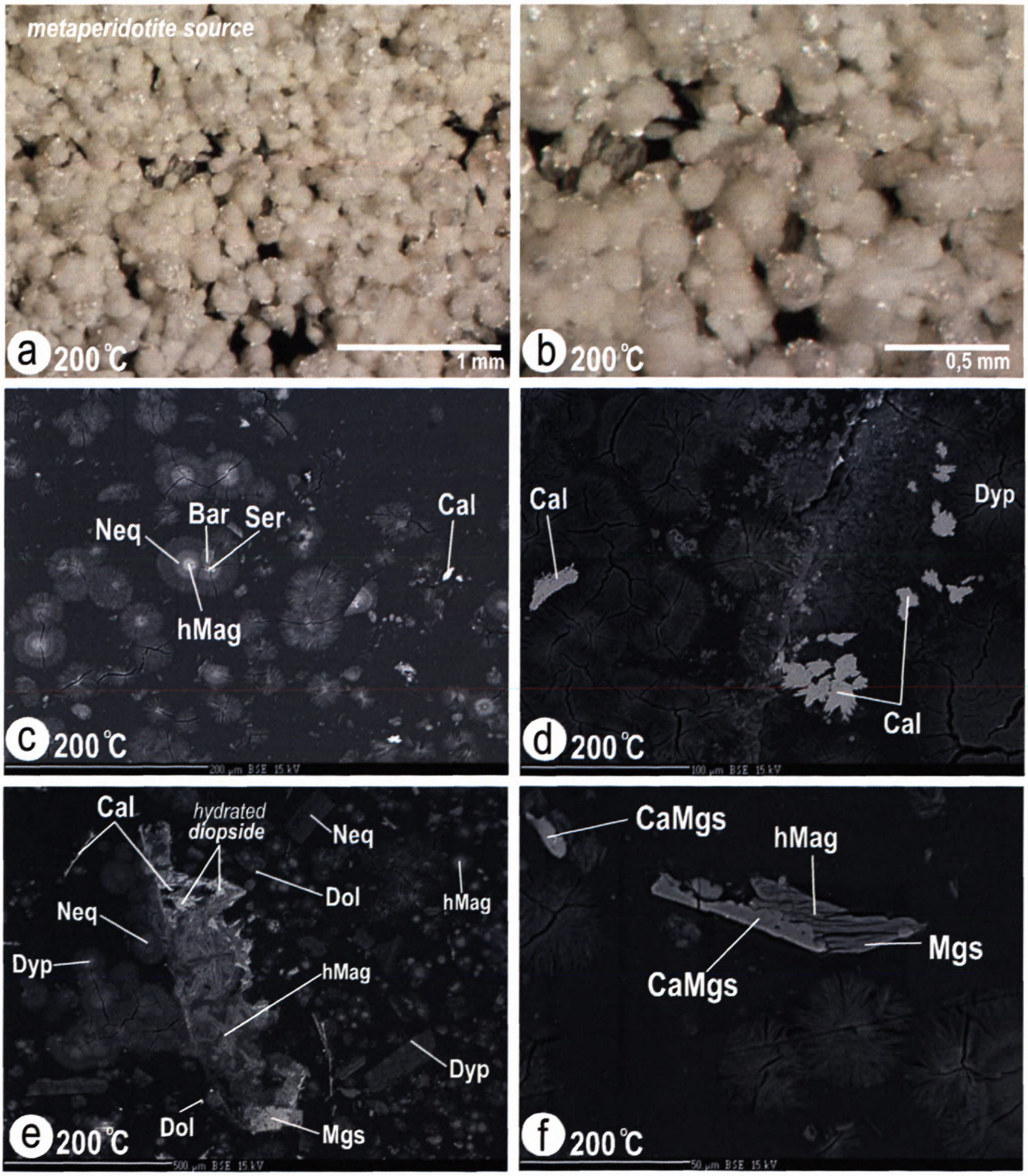

Fig. 7 Products of artificial carbonatization were formed at temperature 200 °C from the metaperidotite – serpentinite source. Sample HO-2., a) and b) spherical form of hydromagnasite (hMag), nesquehonite (Neq), barringtonite (Bar), sergeevite (Ser) and dypingite (Dyp) in binocular loupe, c) zonal grains 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 inage., e) diopside replaced by calcite, by hydromagnesite, by dolomite (Dol) and magnesite (Mag). Initial chrysotile (serpentine) was replaced by nesquehonite, hydromagnesite and dypingite. Back-scattered electron image., f) hydromagnesite, Ca magnesite (CaMag) and magnesite in back-scattered electron image.

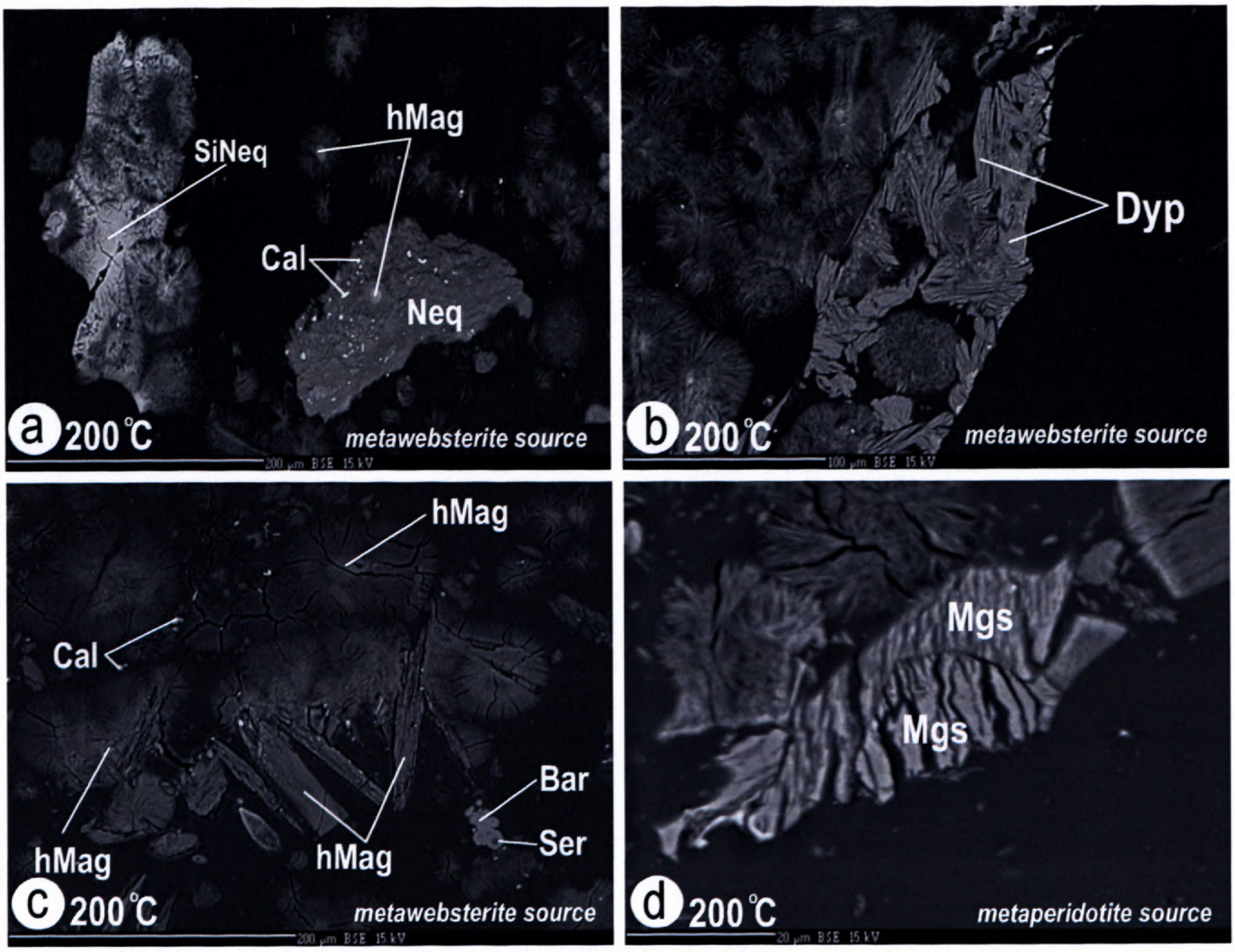

Fig. 8 Products of artificial carbonatization were formed at the temperature 200 °C from websterite source (a,b,c,) and from metaperidotite source (d). Samples RU-1, RU-2 and HO-3., a) hydromagnesite (hMag) nesquehonite (Neq), Si nesquehonite (Si Neq) and calcite (Cal) in back-scattered electron image., b) enstatite grain replaced by dypingite (Dyp). Back-scattered electron image., c) calcite, idiomorphic and zonal grain of hydromagnesite, spherical form of barringtonite (Bar) and sergeevite (Ser) in back-scattered electron image., d) magnesite (Mgs) in back-scattered electron image.

nate 902 kg of CO_2 if the volume density of metawehrlite is 2.57 kg/m^3, or 1 053 kg when its volume density reaches 3.0 kg/m^3. Completely serpentinised wehrlite exhibits the same volume density as the serpentinised peridotite ($\rho = 2.57$ kg/m^3).

The peridotite carbonatization process in conformity with reaction 8 at temperature 160 °C as well as 200 °C consumes 1 174 kg of CO_2, alternatively, 1 006 kg of CO_2 in 1 m^3 of rock in dependence on minimum, or maximum substance of serpentine group in peridotite. According to the same dependence balanced in reaction 9, the 1 m^3 of metawebsterite eliminates 1 078 kg of CO_2 or 924 kg of CO_2 similar to the metaperidotite ability at the same temperature 200 °C. 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, metawehrlite and metawebsterite the consumed weight of carbon dioxide ranges from 902 kg to 1 264 kg and does not depend neither temperature condition of artificial carbonatiztion nor the type of the source serpentinite. Gradual temperature increase from 50 °C through 160 °C to 200 °C has influence to higher participation of carbonates (calcite, dolomite, magnesite) at the expense of acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite). Acid carbonates preferably grow at temperature 50 °C while higher temperatures serve as a suitable environment for carbonates formation.

6. Conclusion

The capability of metaperidotite (locality Komárovce – Hodkovce), metawehrlite (locality Jasov) and metawebsterite (locality Rudník) to eliminate an industrial CO_2 emissions have been verified by the experimental study of artificial carbonatization. Laboratory tests have been carried out at prepared samples of ultramaffic rocks from above mentioned localities. Serpentinite was mixed with water by temperature 22 °C, when was changed the pressure of carbon dioxide from 0.1 to 0.3 MPa and the time from 5 to 20 hours during reactions. The acid carbonates (nesquehonite, barringtonite, dypingite, hydro-

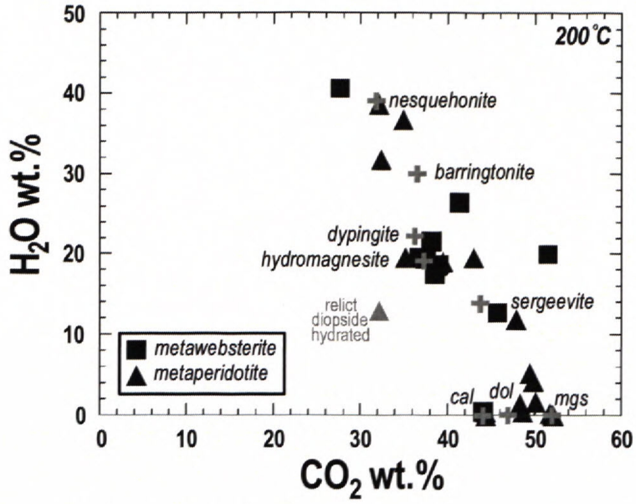

Fig. 9 Variation of H_2O and CO_2 in coexisting acid carbonates: nesquehonite, barringtonite, dypingite, hydromagnesite, sergeevite and carbonates: calcite, dolomite and magnesite. These minerals were formed during artificial carbonatization at temperature 200 °C from the metaperidotite source (sample HO-2) and from metawebsterite source (sample RU-1 and RU-2). Grey plus – H_2O and CO_2 contents in end member minerals: cal – calcite, dol – dolomite, mag – magnesite. Grey triangle – H_2O and CO_2 content in hydrated diopside.

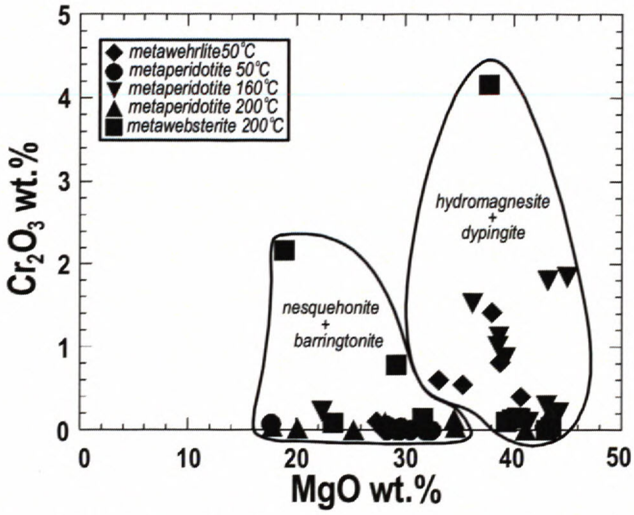

Fig. 11 Variation of Cr_2O_3 and MgO in nesquehonite, barringtonite, dypingite and hydromagnesite. Cr_2O_3 indicates molecule stichtite presence $Mg_6Cr_2(OH)_{16}(CO_3).4(H_2O)$ in these minerals.

magnesite), as well as carbonates (calcite, dolomite, and magnesite) crystallized from filtrate with pH value about of 8, during 4 – 24 hours (the dependency on the various temperatures).

This group of new minerals crystallized according to following reactions:

$$\text{serpentine} + \text{3CO2} + \text{6 H2O} \xrightarrow{50^{\circ}\text{C}+\ 0.1\ \text{MPa}\ CO_2} 2\ \text{nesquehonite} + \text{barringtonite} + SiO_2 \qquad (6)$$

$$2\text{serpentine} + 5\ CO_2 + 4\ H_2O \xrightarrow{50^{\circ}\text{C}+0.1\ \text{MPa}\ CO_2} \text{nesquehonite} + \text{hydromagnesite} + 2SiO_2 \qquad (7)$$

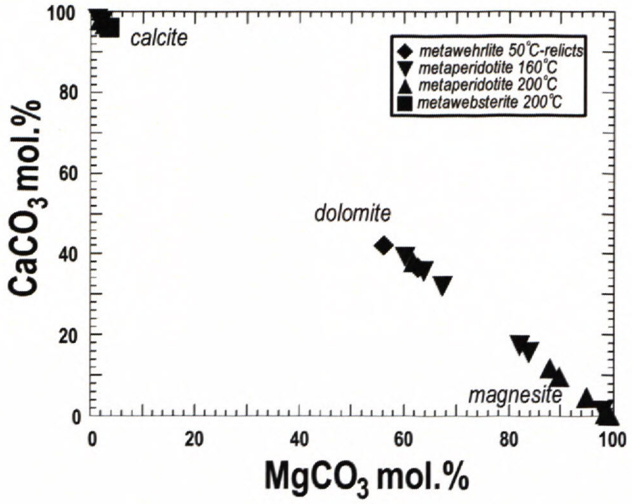

Fig. 10 Variation of $CaCO_3$ and $MgCO_3$ in carbonates. These minerals crystallized at the expenses silicates in various mantle rocks. Dolomite and calcite are relicts of the source metawehrlite, stable at 50 °C.

$$\text{serpentine} + \text{diopside} + \text{olivine} + 6CO_2 + 3H_2O \xrightarrow{160\ ^{\circ}\text{C or } 200\ ^{\circ}\text{C}\ +0.1\text{MPa}\ CO_2} \text{hydromagnesite} + \text{magnesite} + \text{calcite} + 5SiO_2 \qquad (8)$$

$$\text{serpentine} + \text{diopside} + \text{enstatite} + 6CO_2 + 6H_2O \xrightarrow{200\ ^{\circ}\text{C} + 0.1\text{MPa}\ CO_2} \text{hydromagnesite} + \text{nesquehonite} + \text{calcite} + 6SiO_2 \qquad (9)$$

The reactions 6, 7, 8 and 9 served as the base for CO_2 weight calculation that resulted to the final conclusion - how many kg of carbon dioxide is capable 1 m^3 of serpentinite to bond in its volume, during different temperature regimes. In comparison of ideal weight of CO_2 liquidated in 1 m^3 of metaperidotite, metawehrlite and metawebsterite the sequestered weight of carbon dioxide from 902 kg to 1 264 kg does not depend neither the temperature condition of artificial carbonatization nor the type of the source rock. The gradual temperature increases from 50 °C through 160 °C to 200 °C has influence to higher share carbonates formation (calcite, dolomite, and magnesite) at the expense of acid carbonates (nesquehonite, barringtonite, dypingite, hydromagnesite). Acid carbonates are dominating by temperature 50 °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.

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CO_2 sequestration by carbonatization: Origin of new stable products using serpentinite and their potential use in industry

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Abstract. Article presents several methods of CO_2 sequestration with the main emphasis on mineral carbonatization. The main principles of this way of liquidation of industrial CO_2 – direct and indirect method of carbonatization are described with stating of general factors influencing the acceleration of carbonatization.

The carbonatization for CO_2 liquidation was tested using serpentinite from localities Rudník, Hodkovce and Jasov in Slovakia. The laboratory pilot tests have demonstrated that new, solid and high purity products of carbonatization can be prepared from samples of these localities after their granular and thermic modification at particular P-T conditions with subsequent crystallization of carbonate minerals from filtrates.

The new products based on serpentinite were produced in relatively short time of several hours. Originated carbonate minerals – nesquehonite, hydromagnesite, less barringtonite and dypingite – have good use in various branches of industry, e.g. for white anorganic filling agents.

Key words: serpentinite, carbonatization, CO_2, P-T conditions, filtrate, crystallization, carbonates

1. Introduction

Sequestration of CO_2 is defined as catchment, deposition and storage of CO_2. It can be done by physical method (e.g. geological storing), chemical method (e.g. mineral carbonatization) and biological method (e.g. reforestation – photosynthesis of chlorophyll of green parts of the plants with CO_2).

CO_2 sequestration by mineral carbonatization represents safe method for liquidation of industrial CO_2, based on chemical reactions of active components of rocks, resp. waste, with CO_2, resulting in origin of stable and solid products - carbonates, eventually further inert compounds not loading living environment.

The first remark about mineral sequestration was given by Seifritz (1990), and later discussed and developed by Dumsmore (1992). The details and foundation for contemporary investigation have been carried out by Lackner et a. (1995). Since there was possible to pursue quite intensive development in this field. However, it is not a subject of our contribution, to produce overview about this technology. Nevertheless it is fruitful to mention the research by Goff and Lackner (1998), Lackner et al. (1997, 2002, 2005), O`Connor (2000), Zevenhoven and Kohlmann (2002), Zevenhoven and Kavalauskaite (2003) and many other researchers.

The carbonatization can be done by two methods – direct and indirect. Using the direct (one-phase) method the mineral components are added into reaction with CO_2. In indirect method (two-phase) the reactive components are extracted from mineral matrix and successively enter into the reaction with CO_2. In both cases the input minerals can be modified by thermic, chemical, physical-mechanic or mutually combined ways aiming to accelerate the reactions with CO_2 (Uliasz-Bochenczyk et al., 2007).

Carbonatization (mainly the direct method) represents in normal natural conditions very slow process, mainly in the case of natural minerals. Aiming to accelerate the reactions, following factors influencing the reactivity of mineral components with CO_2 must be optimalized technologically:

a) mineral and chemical composition of input rocks (raw material) and activity of their components, purity of CO_2-bearing gas
b) state of input components (solid, liquid and gas phase) and their mutual ratio
c) temperature (T)
d) pressure CO_2 (P)
e) duration (time) of reaction – time of mutual reacting of solid phase with CO_2 (τ)
f) grain-size (fineness), porosity and activity of specific surface of input material
g) modification of input components (thermic, chemical, physical-mechanical, eventually their mutual combination)
h) reaction conditions (static or dynamic)
i) pH of reaction environment and kinds of added reactants (additives, reagents, etc.)
j) density, resp. viscosity of reagent suspension

2. Carbonatization of serpentinite

The laboratory investigation was focused on 5 samples from Slovak localities: Hodkovce (HO-1 and HO-2), Jasov (JA-1) and Rudník (RU-1 and RU-2). Samples were crushed in several steps, homogenized and quartered for chemical silicate analyses (CHA), X-ray diffraction analyses (RTG), differential thermic analyses (DTA) and differential thermogravimetric analyses (DTG).

Tab. 1 states the chemical silicate analyses of investigated samples and Tab. 2 the mineral composition of these samples.

Tab. 1. Chemical composition of input samples

Chemical compound (wt.%)	RU - 1	RU - 2	HO - 1	HO - 2	JA - 1
SiO_2	37.87	39.62	40.21	40.01	40.61
Al_2O_3	2.02	1.71	0.94	0.77	2.46
$Fe_2O_{3\ total}$	6.15	6.36	7.27	8.04	5.74
FeO	0.22	0.11	0.15	0.11	1.09
CaO	4.44	2.02	0.72	0.24	2.61
MgO	34.75	36.47	36.06	36.73	36.23
TiO_2	0.06	0.05	0.02	0.05	0.06
MnO	0.11	0.07	0.08	0.07	0.15
K_2O	<0.01	<0.01	<0.01	0.02	0.01
Na_2O	0.01	<0.01	<0.01	<0.01	0.06
P_2O_5	0.01	<0.01	<0.01	0.01	<0.01
Cr_2O_3	0.364	0.355	0.298	0.334	0.363
loss by ignition	13.98	13.03	14.12	13.44	11.41

Samples from studied localities: RU - Rudník, HO - Hodkovce, JA – Jasov

Based on granulometric analyses of investigated samples and their mineralogical evaluation the input grain-size was determined (beneath 1.0 mm). This grain-size class was used for thermic activation, and successively the laboratory reactions of carbonatization were done. Laboratory tests investigated the ability of prepared input samples to react with gaseous CO2 in real time and simultaneously to form qualitative new mineral phases - carbonate products with high chemical purity for potential use in industrial sphere.

The pilot test of samples were done at determined P-T conditions in laboratory rotating reactor with uninterrupted mixing of suspension formed by solid phase – serpentinite and liquid phase – water, with added CO_2. The ratio of solid phase to liquid phase was 1:5. The duration of carbonatization reactions was within the range 5-20 hours at room temperature and CO_2 pressures 0.1–0.3 MPa.

At the end of reaction the solid phase was separated from liquid phase by sedimentation and the precipitate was separated from liquid phase by filtration. Solid phases and precipitates in this phase of research were not investigated in details, but they contained besides the amorphous Mg-Si phase and amorphous Si phase also carbonatic acids and carbonates in amount 5-30 wt.%.

New, highly pure mineral phases crystallized from filtrates at temperatures 50 °C, 160 °C and 200 °C after 4-24 hours. Among these phases prevailed nesquehonite and hydromagnesite, less abundant were barringtonite, dypingite. In small amount there occurred also magnesite, dolomite and calcite grains (Radvanec et al., 2009).

The formation of quantitatively new, solid mineral products with high chemical purity (besides carbonates above 97 %) by carbonatization of serpentinite and following crystallization from filtrates occurred in relatively short time (not more than 24 hours). Originating carbonate components have good preconditions for their use in different branches of industrial sphere (infillings into plastics, paints, paper, binding constituents, rubber, other anorganic infilling, etc.).

3. Results of laboratory tests

The chemical and mineral compositions of new products obtained after carbonatization and crystallization from filtrates of investigated serpentinite samples from localities Rudník, Hodkovce and Jasov in Slovakia are shown in Tabs. 3 and 4.

Because the investigated samples of serpentinite from studied localities have similar chemical and mineral composition differing only by the contents of some chemical and mineral components, the evaluation of prepared new products in this article is presented only in the case of sample HO-2 from locality Hodkovce, containing in the input 80.3 % of serpentinite minerals, but only 0.4 % of calcite.

Tab. 4 demonstrates that products obtained from serpentinite samples, heated at 50°C, contained 96.9-97.9 % nesquehonite, calcite 0.9-1.5 % and further oxides 1.2-1.7 %.

DTA record of nesquehonite product obtained from the sample HO-2 at 50 °C shows double endoeffect with peaks at 182 °C and 209 °C being accompanied with the loss by ignition 34.9 %, double endoeffect with peaks at 428 °C and 478 °C with loss by ignition 31.3%. Comparison of DTA results with those from chemical analysis has demonstrated that weight loss with peak at 182-209 °C corresponds to loss of adsorption water - 3 H_2O. The weight loss at 428-478 °C corresponds to loss of the functional group - CO_2.

Moreover, Tab. 4 demonstrates that products obtained from serpentinite of investigated samples at 200 °C, resp. 160 °C contained 95.5-97.1 % of hydromagnesite, calcite 1.5-2.6 % and further oxides 1.3-2.1 %.

Comparison of DTA results with the results of chemical analysis has shown that endoeffect with the temperature peak at 321 °C corresponds with the loss of 19 % bounded water in the form of OH groups and own adsorption water - $4H_2O$. The loss of weight 35.6 % with the peaks of endoeffect at 433 °C and 481-520 °C corresponds with the loss of functional group - CO_2.

4. Conclusion

Serpentinites from localities Rudník, Hodkovce and Jasov in Slovakia can be used for liquidation of industrial CO_2 using the method of carbonatization. The laboratory investigation has manifested that after the granular and thermic modification of samples from investigated localities Rudník, Hodkovce and Jasov in Slovakia at certain P-T conditions the qualitatively new, solid and highly pure products can be prepared by the method of carbonatization with subsequent crystallization of carbonate minerals from filtrates.

The formation of new products on the base of serpentinite occurred in relatively short time of several hours.

Obtained carbonate minerals are potentially usable in manifold industrial branches as white anorganic infilling into plastics, paints, binding constituents, glues, rubber, paper, etc.

The originated carbonate products with steady chemical bounds of CO_2 consisted mainly from nesquehonite, hydromagnesite and less barringtonite, dypingite as well as tiny magnesite, dolomite and calcium grains.

Tab. 2. Mineral composition of input samples

Designation of sample	Mineral component (wt.%)				
	serpentine minerals	olivine + pyroxene	magnetite (maghemite)	calcite	chromite
RU - 1	67.6	19.0	5.0	7.9	0.5
RU - 2	76.6	12.5	6.8	3.6	0.5
HO - 1	77.8	12.6	7.9	1.3	0.4
HO - 2	80.3	9.9	8.9	0.4	0.5
JA - 1	78.5	9.7	6.6	4.7	0.5

Tab. 3. Chemical composition of obtained products

Chemical compound (wt.%)	RU-1	RU-1	RU-2	RU-2	HO-1	HO-1	HO-2	HO-2	HO-2	JA-1	JA-1
p (MPa) - T (°C) reaction time (hour)	0.3-22 5	0.3-22 5	0.1-22 20	0.1-22 20	0.3-22 5	0.3-22 5	0.3-22 5	0.3-22 5	0.3-22 5	0.1-22 20	0.1-22 20
crystal. time (hour) cryst. temper. (°C)	24 50	4 200	24 50	4 200	24 50	4 200	24 50	5 160	4 200	24 50	4 200
SiO_2	0.76	0.99	0.82	1.03	1.35	1.70	0.99	0.84	0.94	1.18	0.94
Al_2O_3	0.08	0.07	0.17	0.07	0.09	0.07	0.16	0.08	0.06	0.14	0.06
$Fe_2O_{3\ total.}$	0.02	0.02	0.03	0.02	0.05	0.05	0.04	0.03	0.02	0.03	0.02
CaO	0.51	1.21	0.63	1.29	0.76	1.37	0.50	0.86	0.93	0.84	1.46
MgO	34.14	42.48	34.90	42.60	34.25	42.54	30.09	42.05	43.14	35.11	42.01
TiO_2	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
MnO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K_2O	0.01	0.02	0.01	0.03	0.02	0.03	0.02	0.03	0.04	0.02	0.04
Na_2O	0.06	0.10	0.09	0.13	0.07	0.13	0.13	0.19	0.10	0.13	0.12
P_2O_5	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.01	<0.01	<0.01	<0.01
Cr_2O_3	0.27	0.299	0.24	0.362	0.09	0.086	0.039	0.19	0.12	0.12	0.18
CO_2	34.00	35.59	36.43	35.80	33.28	34.92	32.70	35.64	35.97	34.75	35.90
loss by ignition	63.92	54.60	62.66	54.16	63.12	53.77	67.80	55.55	54.33	61.87	54.78

Samples from studied localities: **RU** - Rudník, **HO** - Hodkovce, **JA** - Jasov

Tab. 4. Mineral composition of obtained products

Sample designation	Mineral component (wt.%)				
	nesquehonite	hydromagnesite	calcite	other oxides	Sum of carbonates
RU-1 (50 °C)	97.9		0.9	1.2	98.8
RU-1 (200 °C)		96.3	2.2	1.5	98.5
RU-2 (50 °C)	97.5		1.1	1.4	98.6
RU-2 (200 °C)		96.0	2.3	1.7	98.3
HO-1 (50 °C)	96.9		1.4	1.7	98.3
HO-1 (200 °C)		95.5	2.4	2.1	97.9
HO-2 (50 °C)	97.6		0.9	1.5	98.5
HO-2 (160 °C)		97.1	1.5	1.4	98.6
HO-2 (200 °C)		97.0	1.7	1.3	98.7
JA-1 (50 °C)	96.9		1.5	1.6	98.4
JA-1 (200 °C)		96.0	2.6	1.4	98.6

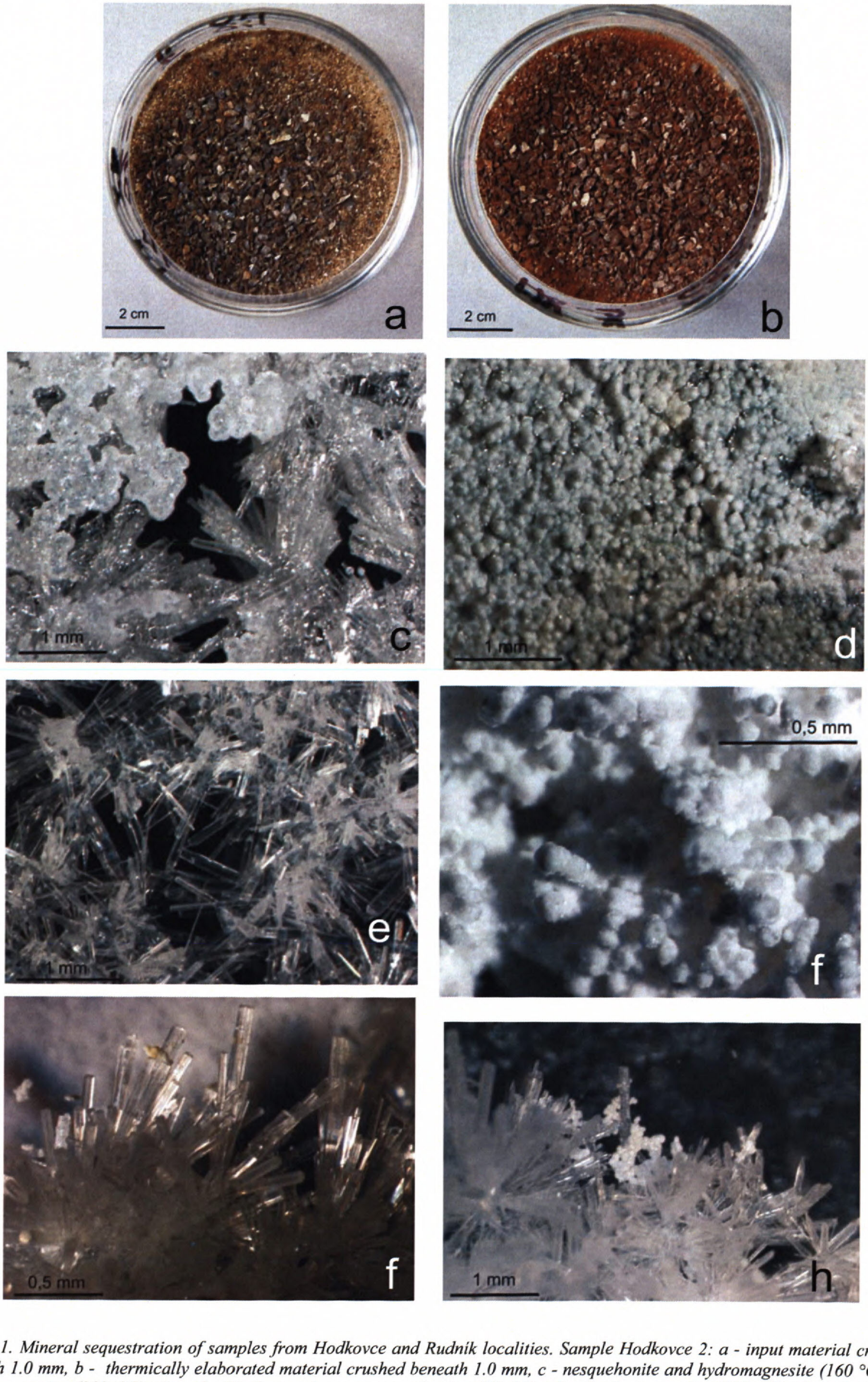

Fig. 1. Mineral sequestration of samples from Hodkovce and Rudník localities. Sample Hodkovce 2: a - input material crushed beneath 1.0 mm, b - thermically elaborated material crushed beneath 1.0 mm, c - nesquehonite and hydromagnesite (160 °C), d - hydromagnesite (200 °C). Sample Hodkovce 1: e - nesquehonite (50 °C), f – hydromagnesite (200 °C). Sample Rudník 2: g - nesquehonite (50 °C), h - nesquehonite (prismatic shape) and hydromagnesite (ball shape; 50 °C).

Tab. 5. Measured X-ray diffraction lattice values for nesquehonite (50 °C) from locality Hodkovce 2 compared with etalon values.

Hodkovce 2 – Nesquehonite (50 °C)					
No.	**Measured values**			**Etalon 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

Tab. 6. Measured X-ray diffraction lattice values for hydromagnesite (200 °C) from locality Hodkovce 2 compared with etalon values.

Hodkovce 2 - Hydromagnesite (200 °C)					
No.	**Measured values**			**Etalon 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	38.320	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

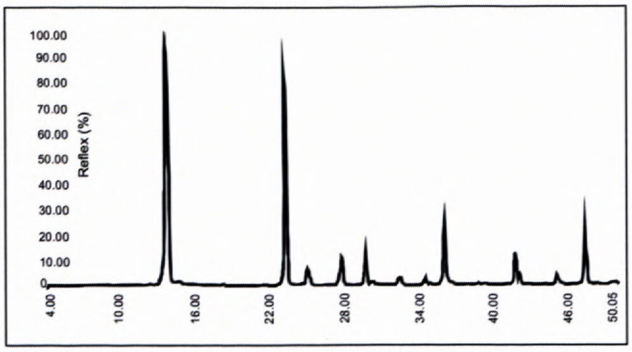

Fig. 2. X-ray diffraction record of nesquehonite (50 °C) from locality Hodkovce 2.

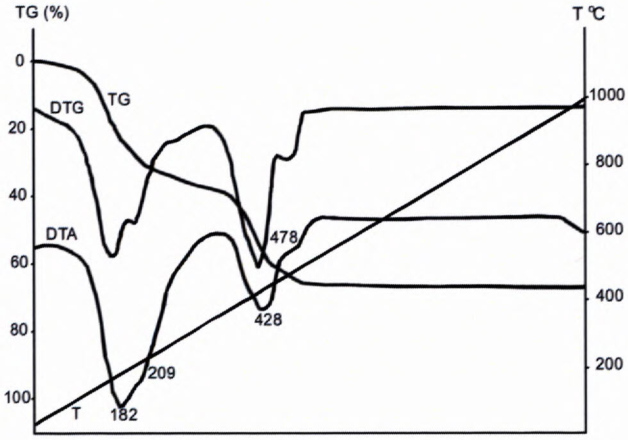

Fig. 3. DTA record of nesquehonite (50 °C) from locality Hodkovce 2.

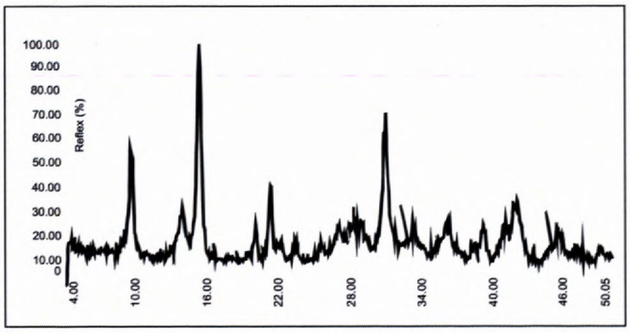

Fig. 4. X-ray diffraction record of hydromagnesite (200 °C) from locality Hodkovce 2.

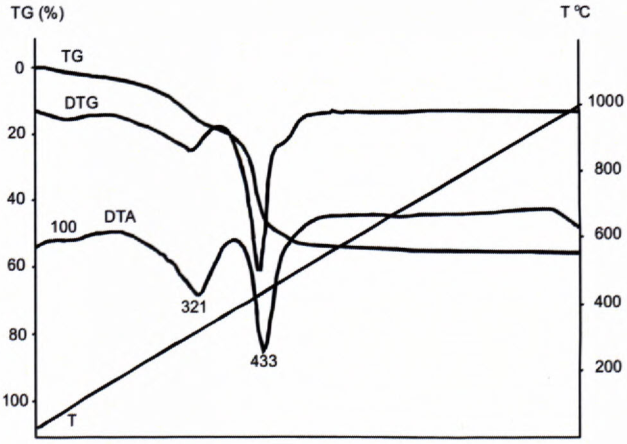

Fig. 5. DTA record of hydromagnesite (200 °C) from locality Hodkovce 2.

5. Acknowledgement

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Case for CO_2 geological storage - site Bzovík Central Slovakia Volcanic Area

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Abstract. Regional aquifers in which is hidden the biggest CO_2 storage potential are covered by younger geological units, often varied genesis and therefore their identification necessitates thorough study of older materials. Such type of locality has been found in South part of Slovakia, where The Central Slovakia Neovolcanics form surface and subsurface feature of landscape. Regional gravity mapping carried out in the sixties of the last century revealed a depression structure in the fundament of Neovolcanics complex. Consecutive deep borehole confirmed this buried structure. Due to convenient lithological development as well as structural - tectonic features, this locality was considered and studied as the possible place for CO_2 storage. A tentative storage capacity calculation was performed, with variable approaches and it was assigned at negative and positive factors in the case CO_2 storage site construction. However it is clear, that in such case this locality in question will have to be suggested to further particular investigation, its applicability is emphasized by proximity of big CO_2 source – the gas transform station Veľké Zlievce, which emissions could be stored here.

Key words: The Central Slovakian Neovolcanic Field, Bzovík Depression, CO_2 storage, capacity calculation, possible scenario discussion

1. Introduction

CO_2 storage conception in geological complexes took place throughout of the last decade in the sphere of carbon dioxide abatement. In term of actual knowledge applicable almost in the whole world, the biggest potential capacity for CO_2 storage is in the deep saline aquifers (Chadwick, et al., 2008). On the other hand, number of credible knowledge about these objects is inadequate and therefore a space for targeted investigation is widely open. However from the lithological point of view, as reservoirs have been almost in any case considered various facies of sandstones in the suitable depths that satisfy supercritical state of this gas, needed for safety and permanent storage. Variability in geological pattern of some areas offers an opportunity to consider as storage site rocks with another geochemical background e.g. carbonates, or not sedimentary (or partly sedimentary) rocks. The most suitable places for CO_2 storage in Slovakia are the marginal, smaller basins of the main or large Pannonian basin. We would like to mention the "so called" hidden possible reservoir, covered by younger geological formations presented by both, sedimentary and volcanic rocks. (Fig.1).

Such site has been found out after the reviewing of general geological pattern of Slovakia with older data of geophysical methods and deep structural boreholes as well. This site is situated in the central part of Slovakia, its south zone. There in the vicinity of village Bzovík, a complex of volcanic- sedimentary formation outcrops on the surface (Neogeneous age). Its fundament is created by older stratigraphical units. The object exhibits structural - morphological feature that can be utilized for purpose of our investigation.

2. Geological and Geophysical background

The studied area belongs from geomorphologic point of view to Krupinská upland zone. The density of settlement is not so high – there is only one township site (Krupina) in the framework of Krupina zone. Larger towns are situated at 30 – 50 km to the North – Zvolen, Banská Bystrica.

The locality is geologically created by complex of volcano sedimentary formation which represents part of Inner Molasse in the West Carpathians. Situation of locality is depicted on the Fig. 1.

Sedimentary and volcano-sedimentary complex consists of following geological units:

The **early Molasse stage** is dated to the kiscel and egerian units, which are created by rocks of Buda Paleogene. While the older kiscel is represented on the base by various facies sandstones and sands with intercalation fine – grained conglomerates overburden layers are created by marlaceous silts (schliers) and/or marly claystones. The maximum thickness of this complex is less than 300 m.

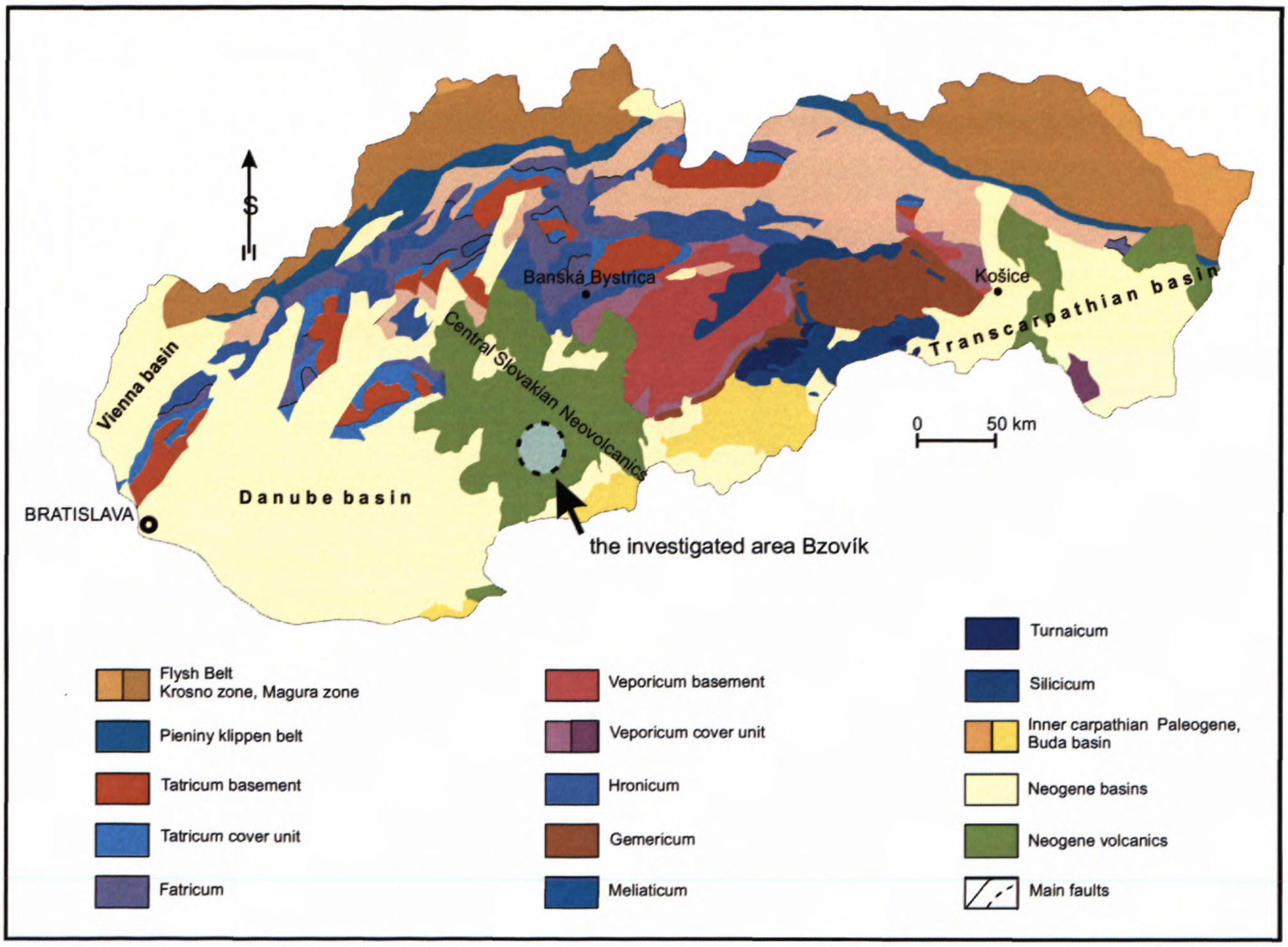

Fig. 1 Transparent tectonic sketch of Slovak Republic (after Biely, 1995) with investigated area location

Overlying Egerian unit reaches thickness 600 – 700 m. Due to its petrographical filling can be considered as suitable trap, because consists of mostly marly silts, siltstones and clays (schliers). Gravels and conglomerates are presented only in the base of this unit. Tuffits layers are occasionally (Vass, et al 1979).

The **main Molasse stage** took time from Eggenburgian to Badenian when main Molasse volcanism took place. The intensive volcanic activity has been learned in the whole scale of Badenian unit. Volcanism had mostly intermediary character – various types of andesites, which are very strongly brecciated. Brecciation reached subsurficial level. Besides of this, volcanoclastic sediments are very porous and permeable.

Pre-volcanic basement in the area is created by Mesozoic rocks (mostly carbonates – limestones and dolomites), which are underlying by crystalline rocks of the Veporicum unit (hybrid granitoids, crystalline schists, phyllits).

Pre-Tertiary fundament is commonly created by the Mesozoic, Late Paleozoic complexes and crystalline rocks. Main portion of Mesozoic rocks can be considered as a suitable environment for CO_2 storage (carbonates). These belong to Late, or Middle Triassic period. Lower Triassic complex is typically present in the shaly facieses, which is practically impermeable horizon for underground water circulation. Similarly or the same characteristics have been learned in the Permian and Crystalline complexes (Vass, et al 1979).

The intensive geophysical investigation targeted at fundament of neovolcanic complex from the old works (Fusán, et. al. 1969), but also from latest ones (Panáček, et al. 1993) has brought several important results that were utilized for this purpose.

Neovolcanic complex itself is a very variegated package of rocks with equally variegated physical properties. The anomaly in question is known since the first basic investigations in the area of Central Slovakian Neovolcanics (Fig. 2). The variations in the density parameter are quite remarkable, but for interpretation purposes an average volume density of this package is usually estimated on the value of 2, 2 g/cm^3. On the contrary, density of fundament is assign at the value of 2, 67 g/ cm^3. That is a reason why the map of Bouguer´s anomalies with above mentioned density has been chosen for depicting of anomaly. (Grand, in Kubeš, et al. 2001). On this base is clear, that the origin of anomaly is not in the volcanic complex, but related to underlying rocks packages – Pre Tertiary basement. A deep structural borehole (GK 4) was drilled for verification of this noticeable anomaly in the late sixties (Konečný, V., et al. 1970) on its area.

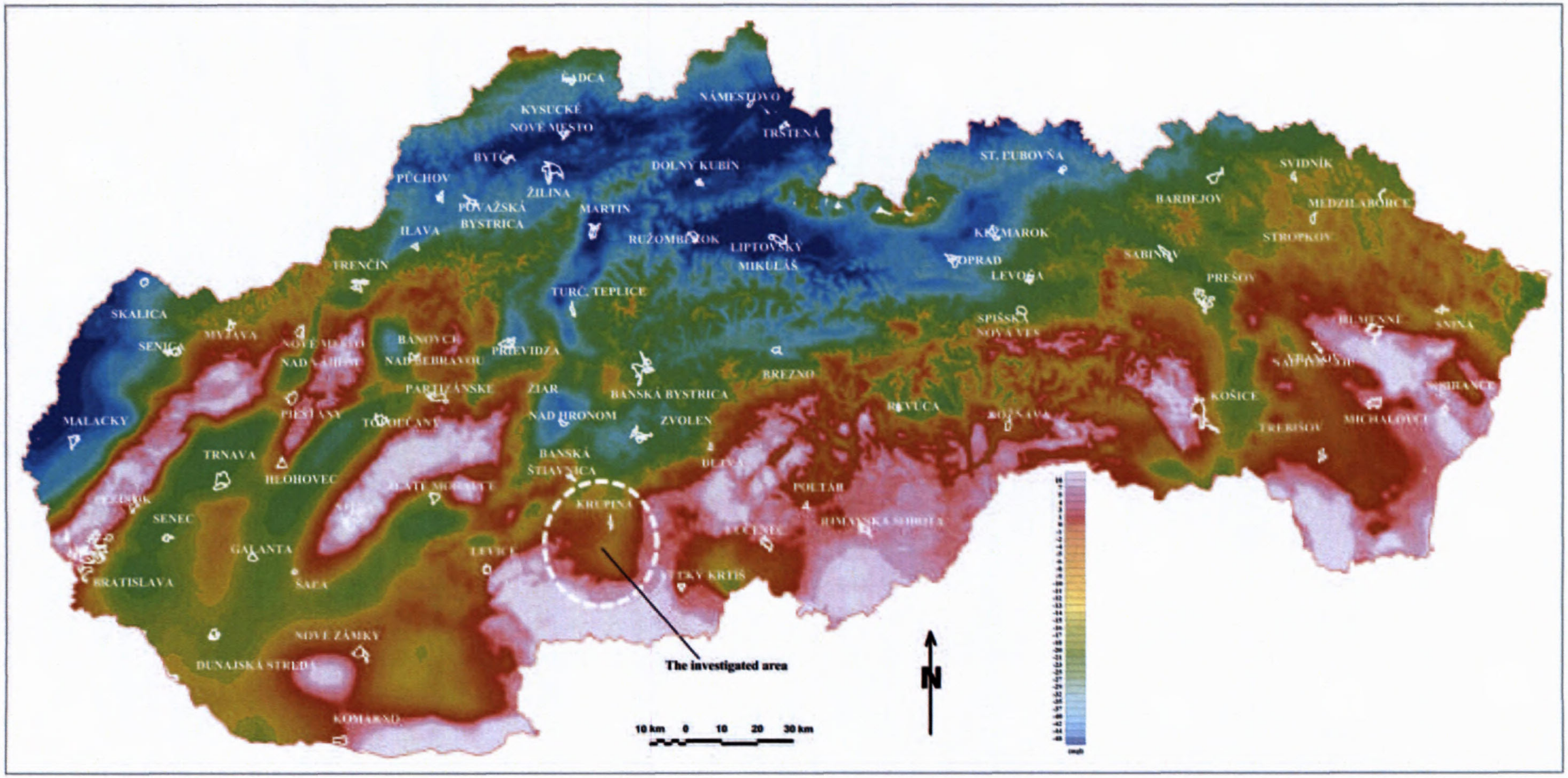

Fig. 2 Gravity map of Slovakia (Bouguer' s anomalies) – reflect of the Bzovík depression (marked area) in the gravity field – vol. dens. 2,2 g/cm3 (processed on the base of Grand, et al. 2001)

3. Results from GK 4 well and their importance for CO_2 storage

The simplified geological profile of the borehole is presented on the Fig. 3.

The uppermost volcano sedimentary unit reaches thickness of almost 1 000 meters. Its typical feature is variability of petrographical filling (tuffs, agglomerates, and tuffits). It is needed to pay attention on its hydrogeological properties, because of its uppermost position in the geological section. This package is defined as a complex possessing mostly intergranular and scarcely joint permeability (in the vicinity of huge faults structures only). Quantity of springs and its yield is not so high. The volcanic complex has a complicated groundwater circuit. It is possible to delineate a shallow subsurface groundwater circuit within the area of Neogene volcanic bound to the cover units as well as to the zone of increased jointing, in which the regimen is distinctly influenced by the climatic conditions. A part of groundwater circulates down to 100–200 m, even deeper, where the discharge regime of the structure reaches equilibrium. The results from extensive drilling in the area of the Krupinská planina Plateau show that the groundwater sources with the greatest yields occur where the tectonic unrest played an important role, i.e. in the lower sections of streams. If the permeability of a rock body is enhanced by tectonic, the yields from wells reach 20 to 30 l/sec at a number of places. The permeability of the volcanic rocks shows some zoning. Due to weathering and to the filling of pores with weathering products the permeability of the upper part of volcanic complex, down to a depth of 30–50 m, is lower. As a result, most wells have the yields below 5.0 l/sec. The Neogene volcanic region is poor in springs. Anyway, results from the deeper part of this complex are not so representative (Malík, et al. 2000).

This package is underlying by lower Paleogene unit, represented by conglomerates, sandstones and less claystones. These rocks possess joint permeability. An intensive brecciation has been observed (Polák, 1978) in this unit. The hanging wall is developed in the form of clays which create the horizon with thickness about 300 m. This layer can be serving as a suitable trap for CO_2.

The lowermost part of the borehole is created by the Mesozoic carbonates complex. The top of this unit is created by package of marl – limestones, marls, shales which is considered as equivalent of Gossau Cretaceous. Subjacent block of carbonates (limestones, dolomites) perhaps belongs to the Middle and Late Triassic. Might be it has suitable environment for CO_2 storage, due to intensive fracturing.

Thickness of the Triassic carbonates is over 300 m. The drilling was stopped in these sequences after reaching of dept 2 108 m. On the base of general geological situation in this locality is presumable that the Permian unit or crystalline rocks should be presented in the footwall of CO_2 reservoir.

The temperature on the bottom of the borehole is 80^0C. The threshold of 31.1 °C for supercritical state achievement is registered in the depth 500 m. The porosity of the carbonates is about 5% (Biela, 1978). Results of well logging were not available in that time. According to Polák, (1978) carbonates are sandy and again intensive brecciated. Data regarding permeability are missing. It means that joint permeability should be important positive input for storage purposes.

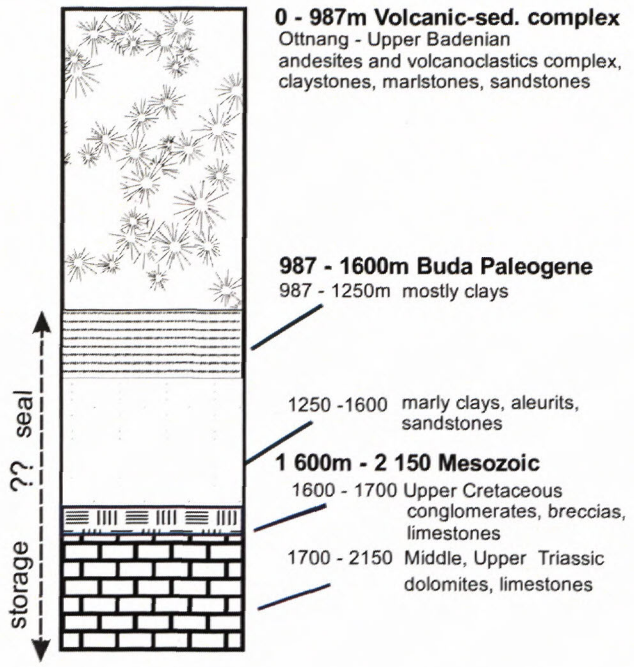

Fig. 3 Simplified geological section of the drilled borehole GK – 4 (after Biela, 1978)

If we summarize the knowledge, obtained from the borehole, we can considerate, that the deep, although point data have been received, which might be granted potential structure for CO_2 storage. From the borehole section is obvious, that the reservoir part consist of the Mesozoic packet and lower part of Paleogene. Clayey horizon should be serving as an effective seal. This structure can be considered as suitable CO_2 storage site if its potential estimated storage capacity is sufficient for adequate absorption of stored CO_2 in relation to neighboring CO_2 emitters and transport facilities.

4. Consideration for storage site extension

A structural – tectonic map of the studied area is given on the Fig. 4. The shown interpretation resulted from gravity, magnetic and geoelectric measurements, followed up with drilling results. It is obvious that remarkable depression structure in the Pre Tertiary basement has been revealed. The structure is prolonged in the NNE – SSW direction and almost from the all sites is circumscribed by elevation of fundament. Average altitudes of the terrain above see level is about 400 – 450 meters. It means, that isoline (isohyps) of basement with the depth 600 m is sufficient criteria for reservoir extension assessment, regarding super – critical temperature achievement (these areas are depicted on the Fig. 4 by blue color.) The studied object can be considered as a local (?) aquifer.

Krupinská depression is bounded by very expressive faults with directions NNE – SSW. From the genetic

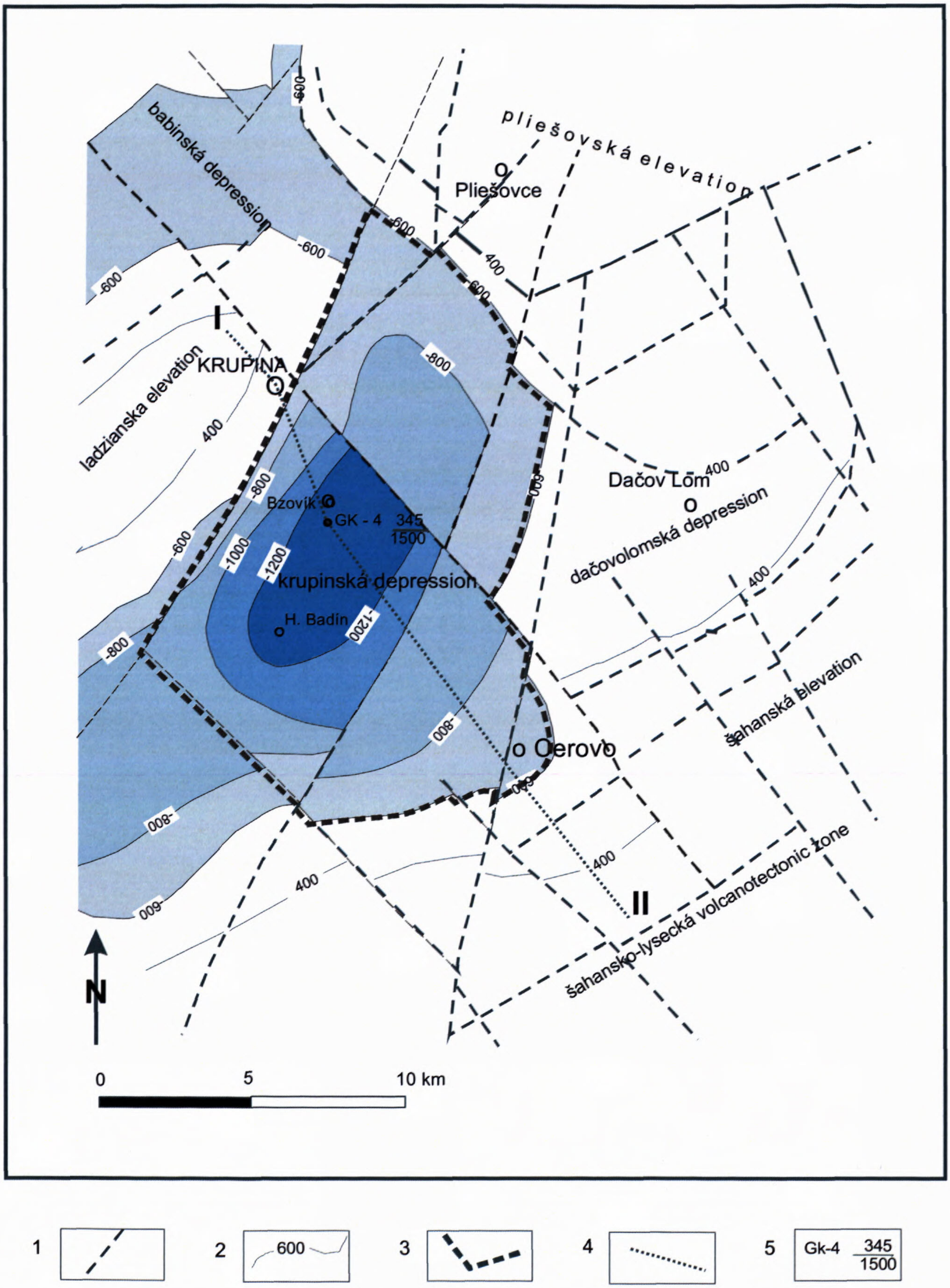

Fig. 4 Structural – tectonic map with depth of pre – Tertiary basement (adapted after Konečný, et al., 1988)
Explanation: 1 – faults, 2 – isohyps of basement bellow sea level, 3 – probable storage site extension (plan), 4 – cross section line, 5 – the borehole altitude/basement depth

viewpoint it had been created before volcanic event and shaped during volcanic activity. There is a premise (Konečný, et. al. 1998) that faults were active even after finishing volcanic phase. Several faults with direction NW – SE slice the fundament into partial blocks. These geological phenomenons are very important input for CO_2 storage from. The steepest fault boundary is toward Krupina town (the Ladzianska elevation). Equally boundary to the North is expressive (the Ladzianska elevation). Demarcation to the East is not so steep (Šahanská elevation), while the Southern part is practically open. An additional investigation about the packing of these faults is needed, because particular information about wishing colmatage is not available, equally as lithological characteristic neighboring rocks.

Overburden cap rocks should be sufficient for trapping, but in any case is necessary to check tectonic situation, because the fault tectonics was active even after the end of volcanic activity (Konečný, et al. 1998).

Beside of this only physical trapping was assumed, even though is obvious that due to carbonate composition of reservoir rocks a chemical trapping certainly will play substantial role by potential storage of CO_2 in increasing storage site capacity.

An objective geological section is depicted on the Fig. 5. Due to borehole result the Mesozoic carbonate body filled the bottom of depression. The depth of carbonate footwall is unknown and can vary within interval of several hundreds meters. The rocks complex is created mostly by dolomites often brecciated, with marly limestones intercalation. This sedimentary unit has Middle and Upper Triassic age (Polák, 1978). The top of carbonate complex is developed in the form of sandy limestones which age is considered as Jurassic. (this level is not shown on Fig. 5 due to small thickness). The depicted Triassic carbonate complex can be suitable reservoir for CO_2 storage purposes.

In the Paleogene base (the Buda Paleogene) is developed huge complex of detritus carbonates rocks – conglomerates, breccias, sandstones and sandy limestone with total thickness of about 500 m (Vass, et al. 1979). This sedimentary level is another potentially convenient target for CO_2 sequestration. We suppose that the petrographical heterogeneity is very high as well as probable lens development, what are factors that decrease theoretical efficacy of complex in question, originally derive from its immense thickness. The uppermost part of Paleogene is presented by the clay complex with thickness of 300 m in the borehole, which could be served as suitable sealing subject. Its integrity development in the whole area from thickness and petrographical point of view is the imperative condition for existence of CO_2 storage side.

The volcanic – sedimentary complex, which covers the above described sedimentary succession, according to our present-day knowledge, has not substantial meaning for sequestration purposes.

This object is a typical example of structure which can be considered as suitable storage site from the first, initial estimation. Many important data are missing that is a reason, why the calculation volume was accomplished by volumetric approach with the simple formula given by Brook, et al., (2003). In the other words – it is useless to estimate unknown needed parameter, controlled by effort to achieve maximum precise result. There are proves from practice, that real construction, or calculation is facilitated only in these cases, when tangible results from drilling, or other works are available (Wűrdemann, 2008).

5. Discussion

The main goal of this part of contribution is to point at some ambiguity and "weakly or not certain places" that influence at our consideration.

- *Capacity calculation*

The data listed in the Tab. 1 assign that fact, that lesser final result dispersion is achieved by mistakes in geometrical factor assessment, however relative interpretation mistake can reach level far above 100%. Similarly CO_2 density in spite of possible variation does not influence final result in a broad scale. The most significant parameters for final capacity calculation ambiguity are porosity assessment and particularly sweep coefficient. Even in cases, when porosity values are available, often scarcely represent all variations caused by heterogeneity of reservoir horizon. The dominant parameter is though sweep coefficient. Value of this is incorporated to the process of capacity calculation, but without practical knowledge, or at least practical data from similar geological units this value is "so called" specialist's estimation, but sometimes seemed to be from the sphere of fantasy. Presented Tab. 1 is clear evidence of this fact. Differences among calculated capacities regarding this "elective" value can be source of serious incorrect evaluation. In our event is interesting factor, that despite of extremely decreased calculated storage capacity - var. 4 in comparison with initial calculation, this amount is still in the scale, which enables the studied case object in question as potential storage site consider. This last calculation (var. 4) was driven on the base of results achieved by May, et al. (2005), when for regional aquifers the coefficient value between 2% – 8% has been utilized.

In this case scarcely may be effective local storage efficiency (Chadwick, et al. 2008), although it is obvious that the object represents "local" structure, due to experience, that heterogeneity in majority similar geological units of the Western Carpathians is very high.

In term of resource pyramids (McCabe, 1988) our position on this locality is on the bottom part of this pyramid representing "theoretical capacity" only.

- *Faults role*

CO_2 leakage along faults will have three behaviors: upward migration from the storage formation along a fault, lateral movement from the fault into permeable layers, and a continued but attenuated CO_2 flux along the fault above the layers (Chang, et al. 2008).

If typical structural anticline hydrocarbon trap is developed with sufficient thick and impermeable containment, carbon dioxide is gradually concentrated per consequence of its buoyancy within the top of structure (vault dome ore arch), which is natural seal.

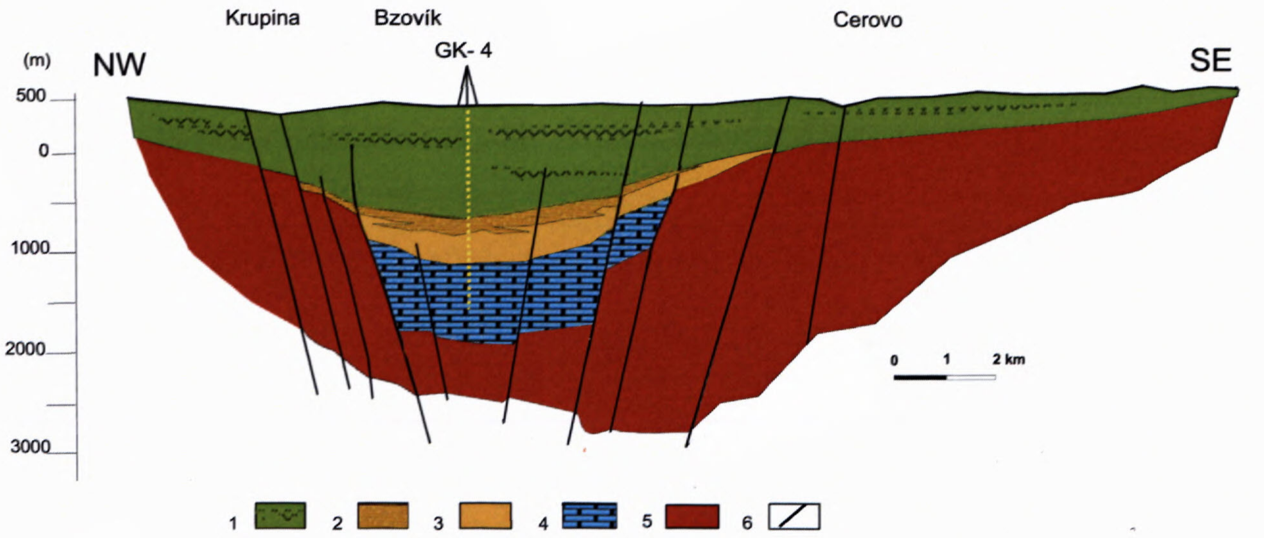

Fig. 5 The objective geological section I – II through the investigated area
Explanation: 1 – volcanic - sedimentary complex (andesites, volcanoclastics, sandstones, claystones, marlstones), 2 – Buda Paleogene – clays mostly, 3 Buda Paleogene - sandstones, limestones, aleurits, 4 – Mesozoic - dolomites mostly, conglomerates, breccias, limestones, 5 – PreMesozoic basement, 6 – Faults

Tab. 1 The capacity calculation – input data for the possible CO_2 storage site Bzovík

Capacity Bzovík	**Area extension**	**Thickness**	**Porosity**	**CO_2density**	**Sweep coef.**	**Capacity CO_2**	**Remark**
	(m^2)	(m)		(g/cm^3)		(tons)	
the initialt calcul.	146 000 000,00	200	0,15	0,63	0,30	**827 820 000**	
variation1	170 000 000,00	300	0,08	0,63	0,10	**257 040 000**	
variation2	200 000 000,00	300	0,05	0,70	0,08	**168 000 000**	
variation3	150 000 000,00	200	0,04	0,68	0,06	**48 960 000**	
variation4	120 000 000,00	150	0,03	0,63	0,04	**13 608 000**	61x less than the1st

This presented type of depression had been originated by strike slip faults and probably represents pull – apart type of basin, what qualifies to suppose synform development. The dip and character of internal filling of fault structure are dominant factor by consideration about possibility leakages creation, especially in the marginal part of basin, which are located on the high level, than depression center. This scenario is described by Kumar (2004) and Ozah, et al., (2005). They have shown small effectiveness of residual phase trapping using "inject low and let rise" strategy. When CO_2 is injected low in the aquifer buoyancy forces drive the injected CO_2 upward, since CO_2 is less dense than brine the water in the reservoir. As it rises, a residual phase trapped by capillary forces is left behind.

This is no convenient event, because carbon dioxide with its buoyancy is concentrated in these upper parts of storage site and in the course of injection and even after closing storage site, developed pressure can destructive influence marginal faults and thereby contribute to possible leakages paths creation.

This is a question for the future, but from contemporary position seems to be feasible a manner, proposed by Burton and Bryant (2007). An alternative approach is to dissolve the CO_2 into brine at the surface, then inject the saturated brine into deep subsurface formations. The CO_2-laden brine is slightly denser than brine containing without CO_2, so ensuring the complete dissolution of all CO_2 into brine at the surface prior to injection will eliminate the risk of buoyancy-driven leakage.

It is matter of course that other faults (in the inner part of depression) that taken place on this locality should be in detail investigated.

- *Lithological constrains*

An assumption of continual suitable rocks complexes development does not need to by valid in the whole area, especially in the marginal part of locality. Buda Paleogene can be typical example in this locality, because it is representing of the lagunar, hypersaline environment (Vass, et al. 1979), where development rock complex can exhibit inhomogeneities in vertical and horizontal plane. It is very important fact, regarding trapping rocks development, where effect of possible tectonic influence is additional negative feature. In spite of this fact, we suppose, that the uppermost Paleogene rocks complex - clays with proven thickness almost 300 m should be sufficient impervious environment effective seal. Higher lying volcanic - sedimentary complex consists of several aquiclude members (tuffits, lavas stream), but due to its heterogeneous development heterogeneity do not represent reliable trapping subject.

Other important feature consists in this, that aquifer collector beside of hydro dynamical sequestration can contribute to storage by mineral sequestration manner, namely in the cases, when is partly, or completely created by carbonate minerals. This is event of locality in question, because we suppose that carbonate rocks (limestones and dolomites) create main portion of space which should be serve as reservoir horizon.

6. Conclusion

The example of possible CO_2 storage site, hidden beneath volcano sedimentary cover in the Slovak republic, has been presented in this contribution. The depression in the fundament of young volcanic complex exhibits features (structural-tectonic, lithological, hydrogeological, suitable depths and temperatures, sufficient tentative capacity calculation) following that is possible to qualify it as suitable CO_2 storage site. Even in the most pessimistic estimation storage capacity, this object could be sufficient for CO_2 storage aimed at the big source of carbon dioxide emissions (transform gas station Veľké Zlievce. This emitter with annual production 520 kT (NAPL 2006) can supply possible storage site during at least 20 years even by the negative capacity calculation approach, what is in concordance with contemporary relations in this field. At present time does not being any storage site in the world, where annual amount of stored CO_2 remarkably exceeds limit of 1 Mt and planned life time of reservoir does not exceed 30 years. It is obvious, that our initial consideration can be changed, after carrying out of targeted additional investigation.

It is necessary to emphasize, that chemical trapping was not taken into account, and however it is clear that due to carbonate content of reservoir can influence storage capacity in positive direction.

The location of the area regarding population is suitable; on the other hand, big sources of CO_2 are not available in the nearby vicinity of this area. The main branch of transit gas pipeline is about 15 km to the SE of this region. But in the radius about 100 km we can find several big producers from paper, aluminum industry, as well as exchange gas distribution, which overall annual CO_2 production exceeds value 1,5 mil tons.

From this point of view the locality in question can be a good potential target for possible CO_2 storage, on condition, that supplementary tangible geological works will be realized.

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