

CO₂ geological storage and mineral trapping potential in the Baltic region

A. SHOGENOVA¹, S. SLIAUPA^{2,3}, K. SHOGENOV¹, R. SLIAUPIENE², R. POMERANCEVA⁴,
M. UIBU⁵ and R. KUUSIK⁵

¹Institute of Geology, Tallinn University of Technology, Estonia, alla@gi.ee

²Institute of Geology and Geography, Lithuania

³Vilnius University, Lithuania

⁴Faculty of Geography and Earth Sciences of the University of Latvia, Latvia

⁵Laboratory of Inorganic Materials, Tallinn University of Technology, Estonia

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 CO₂ emissions, in particular as regards the geological sequestration. The smallest among three countries Estonia with 1.3 mln. population produces the highest CO₂ emissions and is among the highest CO₂ 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 CO₂ 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 CO₂ storage. Alternative approaches are suggested for Estonia and Lithuania, focusing on the mineral trapping of CO₂. The immobilization of CO₂ 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 CO₂ immobilization in Lithuania. The other option for Estonia and Lithuania is a transportation of CO₂ to the Latvian structural traps for geological storage.

Key words: industrial CO₂ emissions, CO₂ geological storage, mineral trapping, serpentinites, oil shales, ash

1. Introduction

Global annual CO₂ 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 CO₂ emissions, including the assessment of the potential of geological sinks and mineral trapping. In 2006 all three Baltic countries started inventory of their CO₂ 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 CO₂ emission in Estonia comes from oil shale combustion, while CO₂ 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 CO₂ emissions using mineral sequestration involves the reaction of CO₂ with minerals to form geologically stable carbonates (Goldberg *et al*, 2000). Carbonation of the naturally occurring silicate minerals, such as serpentine and olivine, provides CO₂ 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

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-Bohenczyk et al, 2007) and oil-shale (Kuusik et al, 2001), and also by other industries such as steel industry, municipal solid-waste incineration ashes (Costa et al, 2007), paper-produced industry ash, medical solid-waste incinerator ash (Bacocchi et al, 2006), etc. CO₂ 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 CO₂. 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 CO₂ 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 CO₂ is captured. At this case process needs extra energy for reactor, but there will be no costs for ash and CO₂ transportation.

2. DISTRIBUTION AND TYPES OF STATIONARY CO₂ SOURCES

In 1990 (reference year of the Kyoto Protocol) the Baltic countries produced 48 Mt of GHG emissions in CO₂ 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 CO₂ 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 CO₂ 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 CO₂ in Estonia, 4.8 Mt in Lithuania and 1.9 Mt in Latvia. In Estonia CO₂ 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 CO₂ 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 CO₂ sources are located in the northeast of the country, close to the oil-shale deposits. The largest CO₂ sources in the Baltic countries are "Estonian" and "Baltic" electric power stations producing respectively 9.4 and 2.7 Mt of CO₂ in 2007. The Kunda Nordic cement plant produced

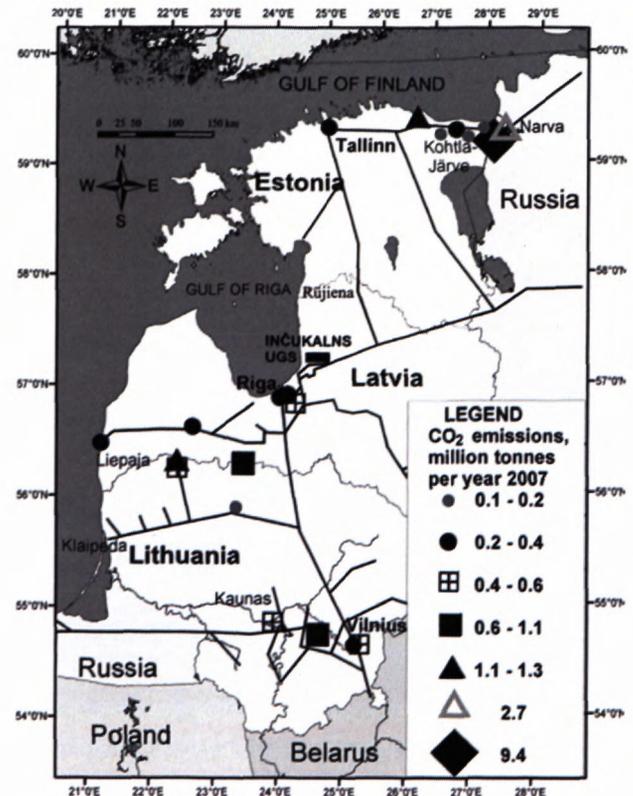


Fig. 1 Large industrial CO₂ emissions (produced in 2007) in Estonia, Latvia and Lithuania registered by European Union Emissions Trading Scheme. Solid lines show natural gas pipeline network. Rectangle shows Inčukalns underground gas storage (UGS).

1.17 Mt of CO₂ in 2007 (0.746 Mt of CO₂ in 2005) (Fig.1) The other concentration of CO₂ sources occurs in the Tallinn region.

In Latvia, the main CO₂ producers are located in the western part of the country. In 2007 the Liepaja metallurgical enterprise emitted 0.356 Mt of CO₂ and three electric power stations in the Riga area emitted 0.567, 0.386 and 0.23 Mt of CO₂ that is close to volumes of 2005.

There are two CO₂ 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 CO₂ in 2007, while the other largest source the Akmene cement plant increased CO₂ production from 0.78 Mt in 2005 up to 1.09 Mt in 2007.

3. PROSPECTIVE CO₂ 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 CO₂ 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)	89	72	58
Fuel combustion in transport	10	27.5	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 CO₂ 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		5	65.7
Lithuania	5.6	9	84.8		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	

CO₂. 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 CO₂ storage. The high water salinity renders these layers unsuitable for use as drinking water or for watering plants. Depending on the formation pres-

sure and temperature, CO₂ can be stored either as high-density gas phase or in a supercritical state ($P > 73.8$ bars, $T > 31^{\circ}\text{C}$).

The Baltic basin contains also a number of oil fields related to Cambrian siliciclastic and Ordovician and Silurian carbonaceous reservoirs. Therefore, the storage of CO₂ 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

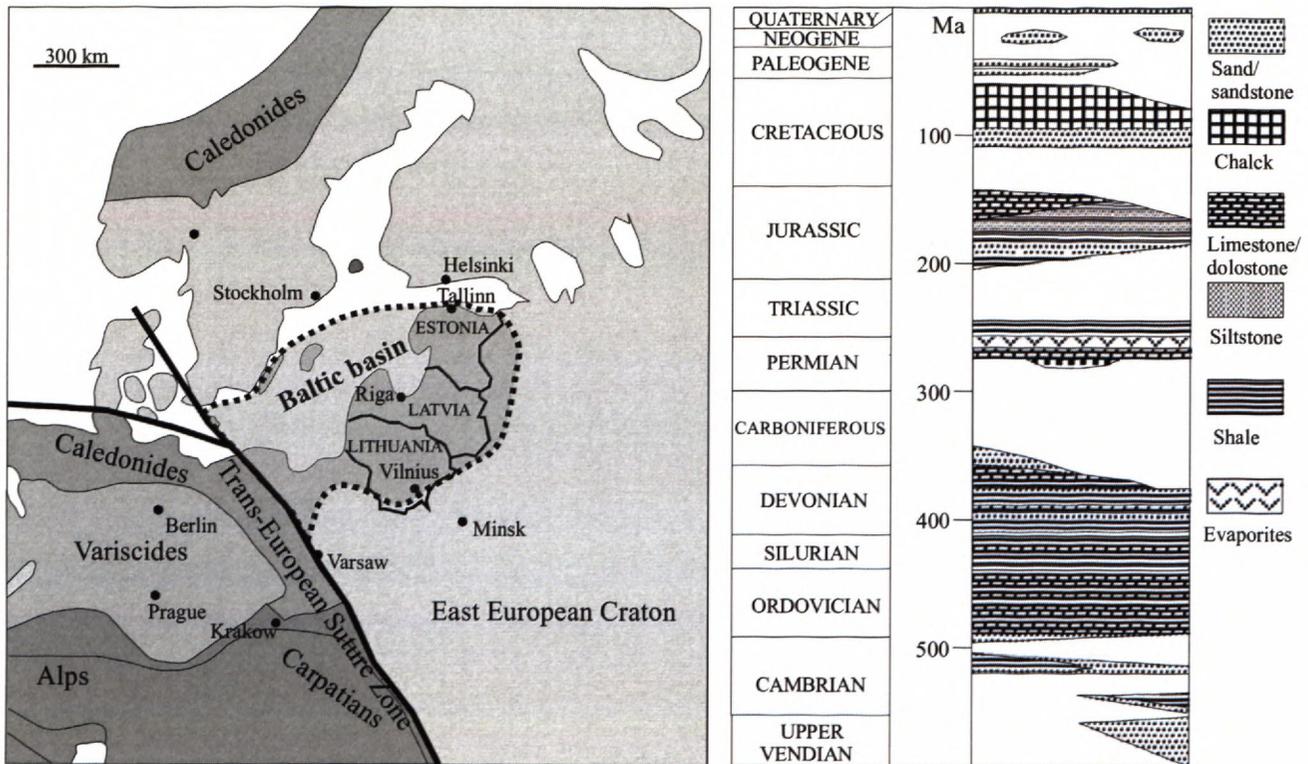


Fig. 2 Geological setting of the Baltic sedimentary basin (basement tectonic sketch map, modified after EUROPROBE TESZ Project).

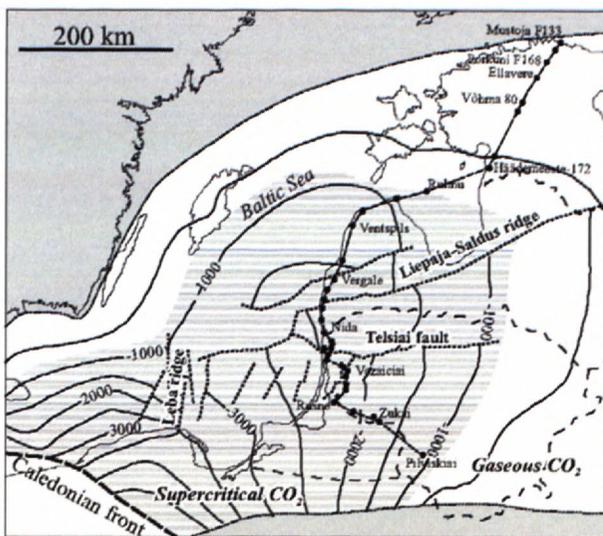


Fig. 3 Depths of top of Cambrian aquifer. The contour lines indicate the depth of the top of Cambrian. The hatched lines show major faults. The P-T fields of gaseous (white) and supercritical (dotted) state of CO_2 are indicated. The line of the geological cross-section shown in Fig. 3 is indicated.

are confined to two major tectonic zones, i.e. the Telsiai 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 (Sliupa 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 (Sliupa 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

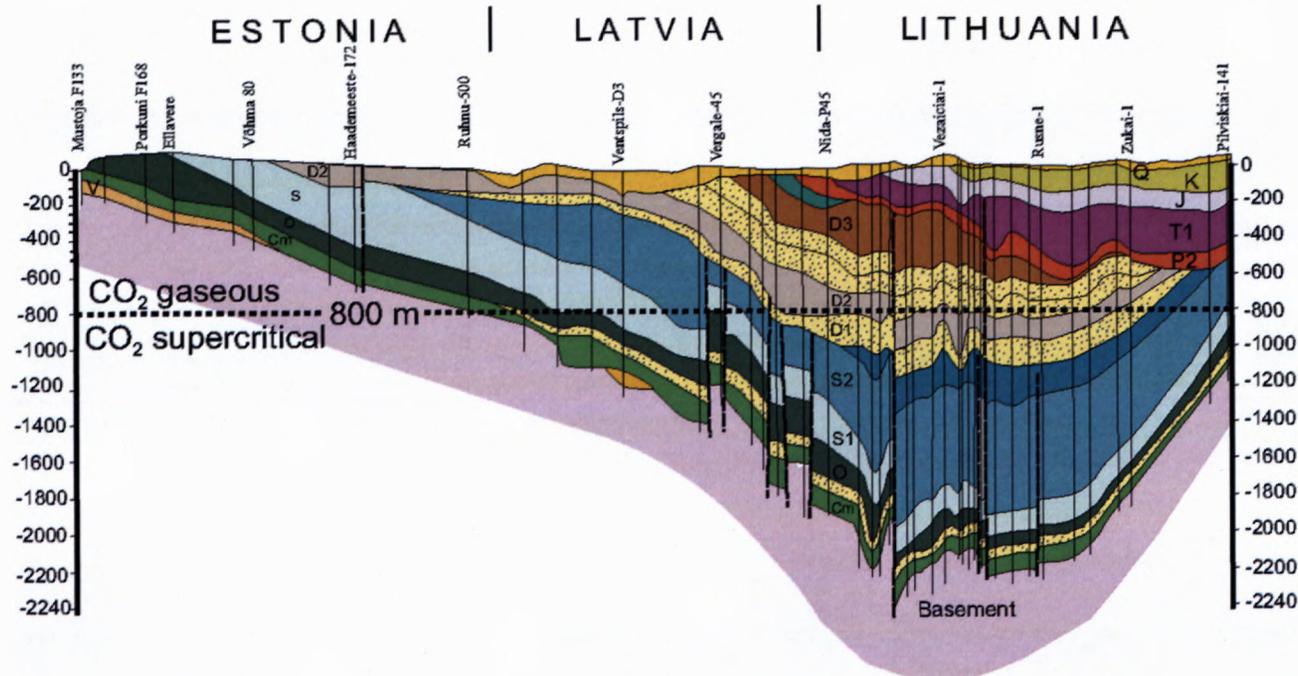


Fig. 4 Geological cross-section across Estonia, Latvia, and Lithuania. Major aquifers are indicated by dots. V – Vendian (Ediacaran), Cm – Cambrian, O – Ordovician, S – Silurian, D1, D2 and D3 – Lower, Middle and Upper Devonian, P2 – Middle Permian, T1 – Lower Triassic, J – Jurassic, K – Cretaceous,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

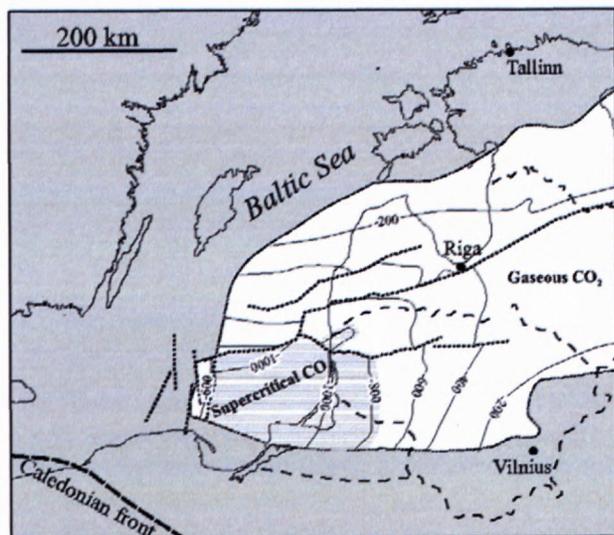


Fig. 5 Depths of top of Pärnu-Kemeri aquifer. The contour lines indicate the depth of the top of Devonian. The hatched lines show major faults. The P-T fields of gaseous (white) and supercritical (dotted) state of CO₂ are indicated.

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 CO₂ 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 CO₂, 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:

$$M_{CO_2} = A \times h \times \varphi \times \rho_{CO_2r} \times S,$$

where M_{CO_2} 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

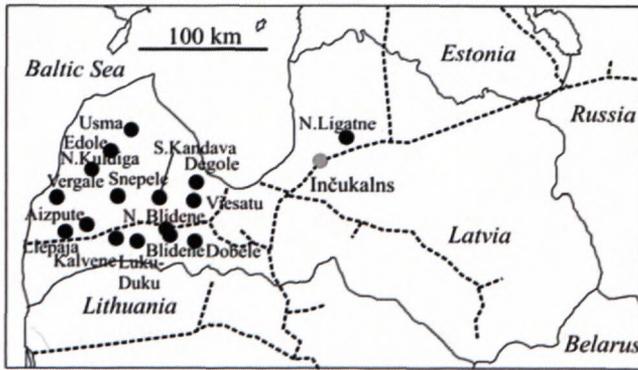


Fig. 6. Major Cambrian aquifer structures (CO_2 storage potential exceeding 10Mt) of Latvia (black circles) and Inčukalns underground gas storage (grey circle). Hatched line shows gas pipelines.

the porosity (typically ranges from 0.25-0.20 in central Latvia and central Lithuania to 0.06 in west Lithuania), ρ_{CO_2} 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 Structures, 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 (Šliupa 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 pres-

sure (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 + CO₂ + H₂O = 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/m³ (Bachu & Adams, 2003), the sequestration potential can be evaluated to reach 5.6 Gt of CO₂ (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 CO₂ sequestration. Alternatively, the serpentinite rocks are abundant in the world and can serve for immobilization of CO₂. 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 CO₂ 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 serpentinites 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 CO₂ carbonation procedure that is as following: *Serpentine* → *Crushing* → *Grinding* → *Screening* → *Magnetic separation (iron ore Fe₃O₄)* → *Reactor (CO₂ solution)*. Only the last operation in this chain is applicable for just the carbonation of the serpentinite.

Roughly, the ratio of the immobilized CO₂ 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 CO₂ production during 200-500 years in the south-eastern CO₂ 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 CO₂ mineral trapping with waste oil shale ash is under development in Republic of Estonia. The concept for abatement of CO₂ emissions in power production based on oil shale ash as sorbent for CO₂ mineralization has been proposed and elaborated (Figure 8). State funded investigations of Tallinn University of Technology, thereby within the framework of Nordic-Baltic project NoCO₂ and under support of energy sector as well as of Ministry of Environment of Estonia shows that the amount of CO₂ which is possible to bind with oil shale ash can cover about 10-12% of the total industrial CO₂ 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 CO₂ 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 CO₂ 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 CO₂ 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 CO₂ per one tonne of ash, and 30-80 kg CO₂ 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 CO₂ 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 CO₂ bound with flue gas could be summarized as

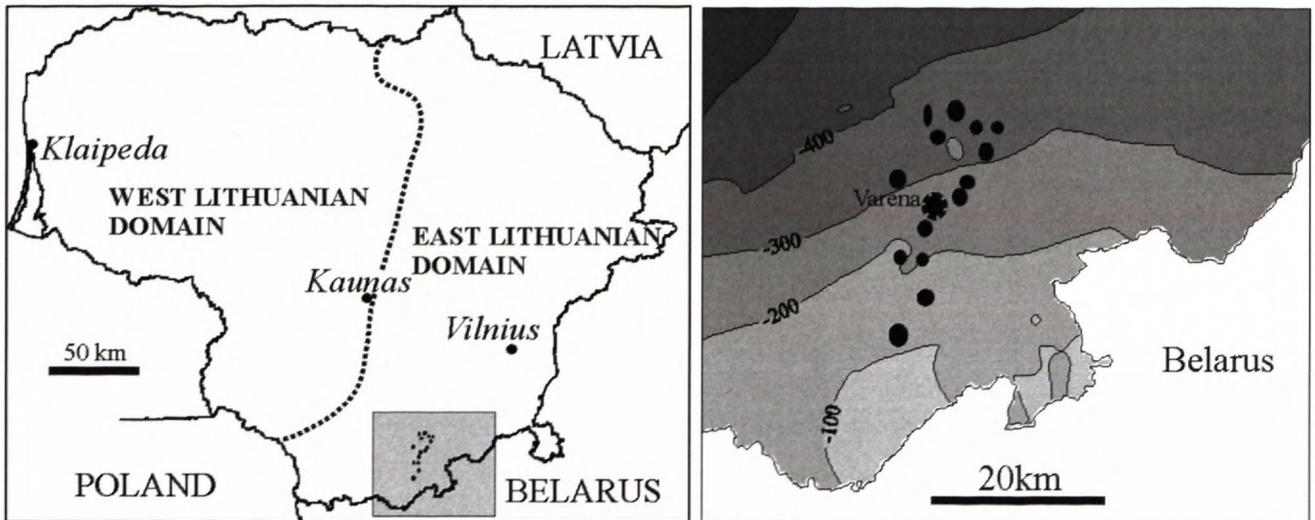


Fig. 7 Left figure shows major lithotectonic domains of the crystalline basement of Lithuania. The Varena Geological Province is shaded. Right figure zooms in the Varena Geological Province. The Varena Iron Ore deposit is distinguished. The depths of the top of the crystalline basement are indicated.

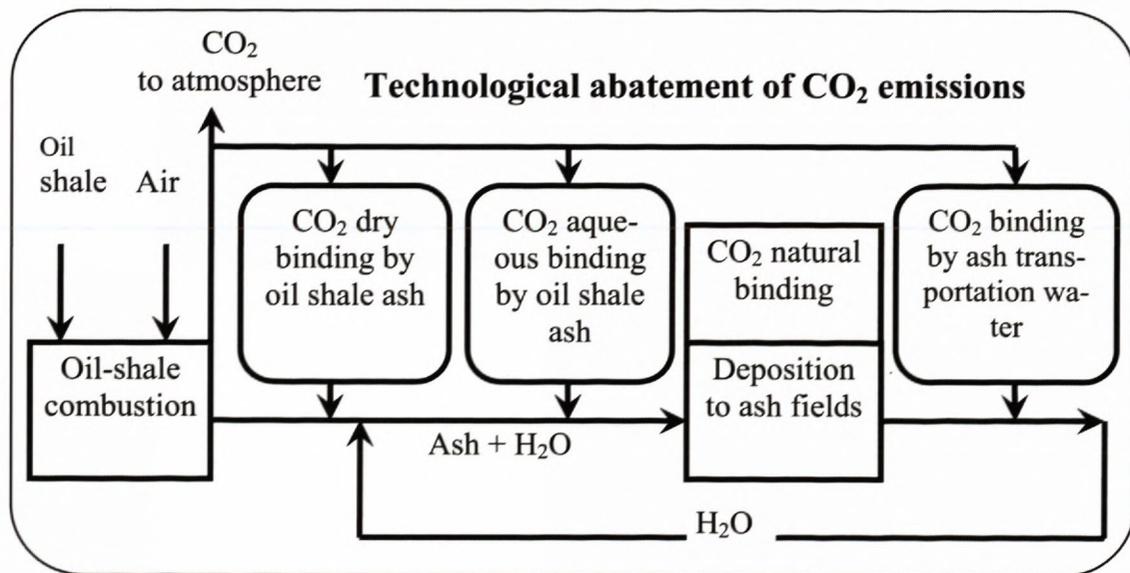


Fig. 8 Concept for CO₂ binding in oil shale-based power production

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

The further studies with concentrated CO₂ 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

CO₂ sources are distributed unevenly in the Baltic countries and the types of CO₂ 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, CO₂ emissions produced by two largest Estonian power plants (12.1 Mt in 2007) exceed the CO₂ produced by all of the Lithuanian (6 Mt) and Latvian (2.89 Mt) stationary sources. During 2007 CO₂ 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 CO₂ storage. However, only Latvia contains structural traps large enough to store the industrial

CO₂ emissions. The capacity of 15 large uplifts have the total capacity exceeding 300 Mt that amounts to more than 150 years of country's CO₂ stationary emissions.

As for Lithuania and Estonia, the transportation of CO₂ 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 CO₂ from flue gas with alkaline ash produced by oil shale combustion and ash transportation water could bind up to 10-12% of industrial CO₂ emissions in Estonia. Application of this technology can solve several environmental problems in Estonia: decrease of CO₂ 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.

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