

# GEO ENeRGY

## Transenergy: transboundary geothermal energy resources of Slovenia, Austria, Hungary and Slovakia

The project „TRANSENERGY – Transboundary Geothermal Energy Resources of Slovenia, Austria, Hungary and Slovakia” is implemented through the Central European Program and co-financed by ERDF. Its aim is to provide a user friendly, web-based decision supporting tool which transfers expert know-how of sustainable utilization of geothermal resources in the western part of the Pannonian basin.

TRANSENERGY addresses the key problem of using geothermal energy resources shared by different countries. The main carrying medium of geothermal energy is thermal groundwater. Regional flow paths are strongly linked to geological structures that do not stop at state borders. Therefore only a transboundary approach and the establishment of a joint, multinational management system may handle the assessment of geothermal potentials and give guidelines for a balanced fluid/heat production to avoid possible negative impacts (depletion, or overexploitation) in the neighboring countries.

Targeted stakeholders are primarily authorities, present and future users and investors, who will get a regional evaluation of geothermal resources in the project area. Assessment will be done by various geological, hydrogeological and geothermal models at a regional scale and on five selected cross-border pilot areas with different geothermal settings, where existing utilization problems have been identified.

### MAIN OUTPUTS:

- multilingual interactive geothermal web-portal containing databases linked to thematic maps, cross sections and models
- geological, hydrogeological and geothermal models for the regional and pilot areas
- scenario models showing estimates on the potential and vulnerability of the cross-border geothermal systems for different extractions of thermal water/heat
- database of current geothermal energy users and production parameters, visualized on transboundary utilization maps
- database of authorities dealing with management and licensing of transboundary geothermal reservoirs
- summary of actual legal and funding framework at the participating countries
- strategy paper evaluating existing exploitation, future possibilities and recommendations for a sustainable and efficient geothermal energy production at the project area

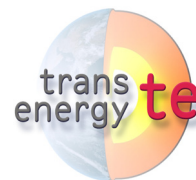
The results of the TRANSENERGY project achieved so far are associated with the overview of utilization of thermal groundwater in the project area, including a database of authorities dealing with



geothermal energy utilization, a database of current users and utilization parameters from 172 users which are visualized on 12 utilization maps and a summary report discussing the various utilization aspects, waste water treatment, monitoring practices, exploited geothermal aquifers and their further potentials. A great variety of geological, hydrogeological and geothermal data to be used for modeling have been collected and uploaded into a harmonized, multilingual database, containing data from more than 2500 boreholes from the 4 countries. Additional investigations (hydrogeochemical analyses, temperature logging, petrophysical measurements) were carried out from areas with poor data coverage and these will also be incorporated into the final expert database, a part of

which will be available to the public in 2012. Geological, hydrogeological and geothermal modelling is ongoing on a supra-regional scale covering the entire project area. The geological model shows the spatial distribution of the most important hydrostratigraphic units, while maps of temperature distribution at various depths characterize the thermal field. This serves a basis for more detailed modelling to be carried out on selected cross-border pilot areas in 2012 and 2013.

Results can be downloaded from the project website (<http://transenergy.eu.geologie.ac.at/>), which provides further information and PR material about ongoing activities.



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Fig.1 Transenergy project area. Within the investigated region (red line) the project focuses on some representative pilot-areas along the borders (thermal karst of Komarno-Sturovo area (HU-SK), Pannonian Central Depression of the Danube basin (A-SK-HU), Lutzmannsburg – Zsira area (A-HU), Vienna basin (SK-A) and Bad Radkersburg – Hodoš area (A-SLO-HU))

# Ex-situ and in-situ mineral carbonation: alternative technology to mitigate climate change

Fixation of CO<sub>2</sub> in the form of inorganic carbonates, also known as "mineral carbonation" was proposed in the USA by Seifritz in 1990 and developed by Lackner in 1995-2003. The thought behind it is to accelerate the natural weathering processes up to an industrially acceptable level. Initially, only natural Ca- and Mg-rich minerals (serpentine, olivine, wollastonite, talc) were considered as CO<sub>2</sub> binders, while several alkali wastes, like steel slag and ashes from power plants were considered later. The main parameters of dry and aqueous CO<sub>2</sub>-binding by natural minerals and process routes were worked out in 1995-2005. At the present time United States Geological Survey (USGS) is working in two areas of mineral carbonation: CO<sub>2</sub> mineral carbonation using ultramafic rocks (peridotite, dunite, serpentinite and picrite) and accelerated weathering of limestone (AWL) ([http://crustal.usgs.gov/projects/CO2\\_sequestration/carbonation.html](http://crustal.usgs.gov/projects/CO2_sequestration/carbonation.html)).

Carbonation of alkaline minerals mimics the natural weathering of rock and involves the permanent storage of CO<sub>2</sub> as the thermodynamically stable form of calcium and magnesium carbonates. Unlike other CO<sub>2</sub> sequestration routes, it provides a leakage-free long-term sequestration option, without a need for post-storage monitoring once CO<sub>2</sub> has been fixed. Mineral carbonation of CO<sub>2</sub> is an exothermic reaction, theoretically allowing a decreased energy penalty for CO<sub>2</sub> capture.

In-situ CO<sub>2</sub> storage involves reacting CO<sub>2</sub> with alkaline minerals to form carbonates. This is possible in mafic (deep flood basalt formations and basaltic lava flows) and ultramafic rocks rich in mineral olivine (peridotites). The concept of CO<sub>2</sub> storage in basalts was proposed by McGrail in 2003 and then developed using laboratory and numerical simulations, resulting in two ongoing pilot projects in USA and Iceland. The porosity of ultramafic rocks is usually much lower compared to sedimentary reservoirs, therefore artificial permeability enhancement through hydraulic fracturing is likely required to support injection of significant amounts of CO<sub>2</sub>. However, brecciated interflow zones in basalts can have good porosity (5-15%) and permeability sufficient for commercial-scale CO<sub>2</sub> injection. Flood basalts also happen to be located in many onshore and ocean regions where conventional saline aquifer storage options are limited (e.g. India).

The Wallula Basalt Sequestration Pilot Project (Big Sky Partnership; DOE, USA) plans to inject up to 1000 tons of CO<sub>2</sub> into the Columbia River flood basalts at a depth of approximately 900 m (Fig. 2). The injection well at the site has an exposed injection zone containing non-potable brackish water, sealed and covered by extremely low permeability cap rocks. The Wallula storage site was studied by seismic surveys in 2007 and the borehole was drilled in 2009 to a total depth 1253 m. Washington State approved the world's first supercritical CO<sub>2</sub> injection permit for a flood basalt test in March 2011. Injection planning is presently in-progress (<http://www.bigskyco2.org/research/geology/basaltproject>). Conservative estimates

for CO<sub>2</sub> storage in the Miocene Columbia River Basalt Group is 10-50 Gt CO<sub>2</sub>, while total capacity of US Basalt Formations is 240 Gt, compared to 2600 Gt in USA Saline aquifers as reported by Dahowski et al. in 2005.

A field scale injection of CO<sub>2</sub> into basalts in Hellisheidi, Iceland, was started in late January 2012 in the frame of the international CarbFix project, a combined industrial and academic research program. 175 tonnes of pure CO<sub>2</sub> were injected at the CarbFix injection site in Hellisheidi, SW-Iceland, over a period of approximately 5 weeks, from late January to early March. A mixture of water and steam is harnessed from 2000 m deep wells at Hellisheidi geothermal power plant. CO<sub>2</sub> from the plant is dissolved in water at elevated pressure and then injected through wells down to 400-800 m, just outside the boundary of the geothermal system. The liquid should react with calcium from the basalt and form calcite. This process

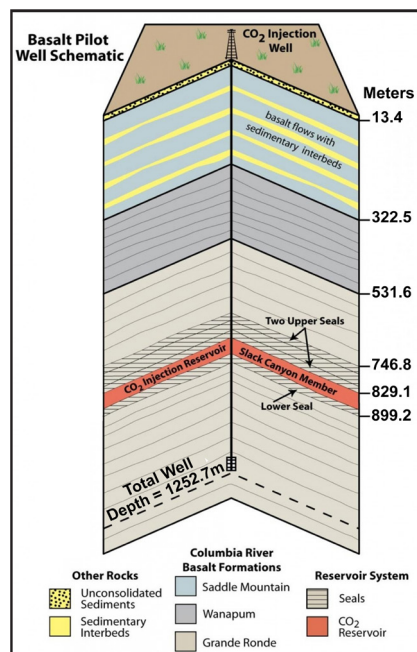


Fig. 2 Stratigraphy surrounding the CO<sub>2</sub> injection borehole at the Wallula Basalt Pilot site. Source: Battelle Pacific Northwest Division, Richland, Washington, USA

occurs naturally and the mineral calcite is stable for thousands of years in geothermal systems. Assuming an average of 10% porosity of basalts at Hellisheidi pilot storage site, the storage capacity is estimated as 12 Mt CO<sub>2</sub>, which is sufficient for 200 years production for the nearest geothermal Power Plant which emits 60000 t CO<sub>2</sub> per year (<http://www.or.is/English/Projects/CarbFix/AbouttheProject>). In situ mineral carbonation projects will need monitoring programs to avoid possible leakage through fractures, faults or abandoned boreholes and metal leaching from the rocks.

The first ex-situ mineral carbonation pilot project combining CO<sub>2</sub> with serpentinite was announced in 2010 in Newcastle, Australia. The two-phase process will react serpentinite and CO<sub>2</sub> to make magnesium carbonate,

which could be used for products such as building materials, bricks, pavers, cement and agricultural additives. There is enough serpentinite in New South Wales to capture carbon dioxide in this way for thousands of years if the technology proves to be feasible on a large scale. The pilot demonstration plant is planned to be built at an experimental site in Newcastle and to provide bulk sample carbonate material to interested product developers by 2012. If the Newcastle trial proves successful a demonstration scale plant is scheduled to become operational by 2016 and an industrial full-scale plant could be available at about 2020 (<http://www.sustainabilitymatters.net.au/articles/41409-Mineral-carbonation-project-for-NSW>).

Ex-situ mineral carbonation using waste materials is also currently studied. This technique can use coal and oil-shale ash and waste water, stainless steel slag from the steel industry, as well as waste products from the cement industry, municipal solid-waste incineration ashes, paper-produced industry ash and medical solid-waste incinerator ash. These options are usually available near the CO<sub>2</sub> emission source, and allow the stabilization and neutralization of hazardous/toxic waste material, with the economic benefit of by-products with high commercial value. The main disadvantages of ex-situ mineral carbonation technology is that the amount of CO<sub>2</sub> which can react with the waste material is not very large. Maximum of 5% of the produced CO<sub>2</sub> amount for coal ash up to 10-12% for Estonian oil shale ash based on fresh ash and waste water (up to 90% of CO<sub>2</sub> is possible to avoid using near deposited old alkaline ash as sorbent). For ex-situ mineral carbonation by geological minerals, large mining works are required, because to fix a tonne of CO<sub>2</sub> requires 1.6-3.7 tonnes of rock. The scale could be the same as the existing mining works in the world and the price for one tonne of CO<sub>2</sub> abandoned could be higher than for Carbon Capture and Storage (CCS). At present, the European Commission has not published any call for projects targeted on mineral carbonation and did not include it in CCS or any other directive. A regulatory framework for wide implementation of mineral carbonation technology is absent worldwide, while mining laws and available regulations for underground CO<sub>2</sub> injection and storage can be applied for in-situ projects. Mineral carbonation technology is considered to be now in research and developing, as well as early pilot phase.



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# Prospects for CO<sub>2</sub> mineralization in Estonia

CO<sub>2</sub> emissions produced in Estonia are among the highest per capita in Europe. Mineral carbonation has been proposed as a means to reducing industrial CO<sub>2</sub> emissions in Estonia, whose energy sector is predominantly (up to 67%) based on oil shale, a locally available low-grade fossil fuel. Estonian oil shale differs from other fossil fuels in its high content of mineral CO<sub>2</sub> in the form of limestone and dolomite. Ash formed during oil shale combustion contains free Ca and Mg oxides (10-30%, depending on combustion technology), and could be considered as a CO<sub>2</sub> binder even via the natural weathering process. An idea suggested by Punning and Karindi in 1996 has been studied intensively by Kuusik et al. since 2001, resulting in two doctoral theses, two patents and a number of scientific publications.

The concept of the CO<sub>2</sub> mineral sequestration in the oil shale waste ashes from Estonian heat and power production has been proposed to reduce CO<sub>2</sub> emissions released into the atmosphere and neutralize alkaline waste ash and water produced during oil shale combustion (Figure 4). The main parameters of the most promising technological ways - for aqueous processes of CO<sub>2</sub> binding via direct (ash suspensions) or indirect (alkaline ash-transportation water) aqueous carbonation of the ash with flue gases and via natural weathering at open-air ash deposits have been elaborated.

Based on multifaceted studies about aqueous carbonation of oil shale ash, a new method for eliminating CO<sub>2</sub> from flue gases by Ca-containing waste material was proposed. The process includes contacting the aqueous suspensions of Ca-containing waste material with CO<sub>2</sub> containing flue gases in two steps: the water-soluble components such as free lime are carbonated in the first step (at pH 10-12) and the components of low solubility (Ca-silicates) are carbonated in the second step (at pH 7-8). According to the experiments 170-290 kg CO<sub>2</sub> could be bound per ton of ash in mild operating conditions (ambient temperature and atmospheric pressure).

Carbonation of alkaline ash transportation waters provided a waste valorization option by production of precipitated CaCO<sub>3</sub> (PCC). Obtained PCC contained 94-96% CaCO<sub>3</sub> and was characterized by a regular rhombohedral structure (which is controlled by crystallization conditions), high brightness (93%) and mean particles size of 4-8 µm

(Figure 3).

The availability of the raw material is more than sufficient, as in addition to the annual

production of waste ash (6 Mt), the waste heaps contain more than 250 Mt of hydrated ash. Also, 10<sup>7</sup>-10<sup>8</sup> cubic meters of Ca<sup>2+</sup>-ion saturated alkaline water is recycled in the hydraulic ash transportation system. An additional advantage of this approach is the neutralisation of the alkalinity of ash offering a possibility for environmentally sound landfilling of waste residue.

It has been estimated that 10-12% of annual large CO<sub>2</sub> emissions produced by the Estonian power sector can be bound by annually produced oil shale ash and waste water.

Future studies also include process modelling in order to estimate the feasibility of the proposed methods compared to the conventional flue gas decarbonization and PCC production methods.

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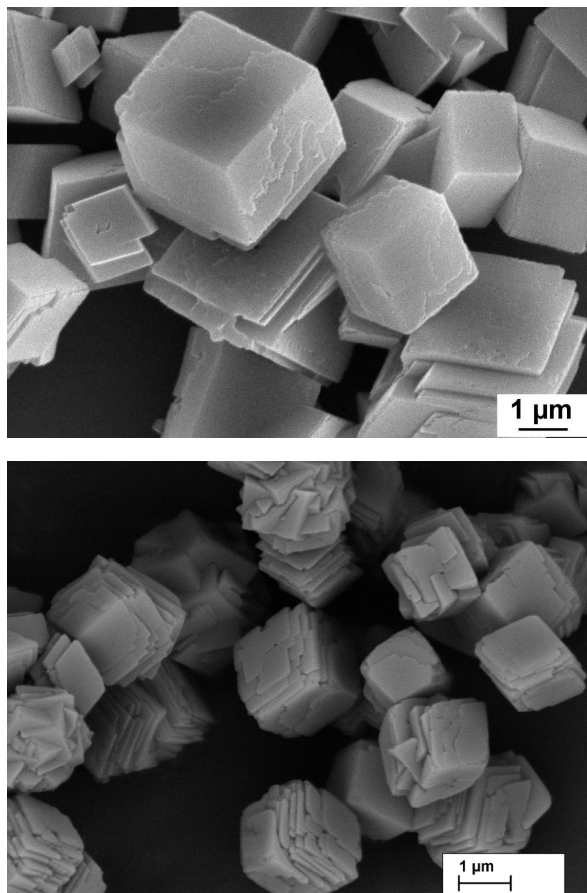


Fig. 3 SEM images of PCC samples formed at different conditions in dispergator-type phase mixer and barboter-type column

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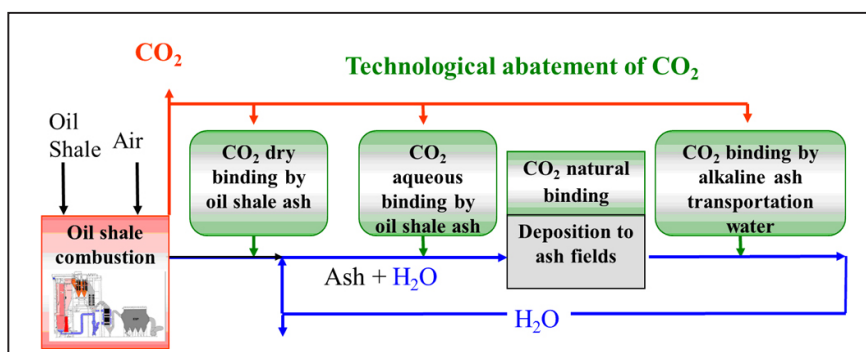


Fig. 4 The concept of CO<sub>2</sub> mineralization in Estonian energy sector

## ENeRG – European Network for Research in Geo-Energy

### ENeRG – European Network for Research in Geo-Energy

is an informal contact network open to all European organisations with a primary mission and objective to conduct basic and applied research and technological activities related to the exploration and production of energy sources derived from the Earth's crust.

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# Recent results on mineral carbonatization in Slovakia

The methodology of mineral carbonation has progressed in Slovakia during last four years. We prefer to use the term „carbonatization“, because the process results in the formation of carbonates. Different materials for binding CO<sub>2</sub>, including rocks and various wastes, were tested. Waste material was represented by fly ash and slags from the energy and heat production industry, as well as an asbestos cement known as eternit. The main requirement for a successful reaction with CO<sub>2</sub> is the presence of Ca and Mg cations in appropriate compounds of reacting samples. The rate of CO<sub>2</sub> reaction with the Ca and Mg components is strongly affected by the prior activation of the tested material. Mechanical, thermal and chemical activation techniques or combination of these methods were applied.

Ultramafic rocks of the serpentinite group (containing 35-40% MgO), mainly represented in East Slovakia, have been used for mineral carbonatization. The optimum laboratory conditions were found at a temperature of 22°C, a pressure of 6 MPa and a stirrer rotation of 300 rpm. After reaction of the material in the high-pressure reactor and filtration of the suspension, two carbonate minerals were formed. Nesquehonite crystallized at 50°C with a purity of 94-98%. Hydromagnesite crystallized later at 200°C with a purity of 91-98% (Fig. 5). The best reaction results were found with samples from the Hodkovce village (Slovakia). The hydromagnesite with a weight yield of 17-22% was formed during a one hour reaction after mechanical-thermal pre-treatment. During the formation of the carbonate product, containing predominantly hydromagnesite at the above-stated conditions, a total of 2.9-3.3 tonnes of serpentinite rock bound one tonne of CO<sub>2</sub>.

Fine-grained fly ash, the product of black (hard) coal burning, was also tested. Prior to artificial carbonatization, 98% of the fly ash had

a grain-size <0.2 mm. The fly ash contained 98.3% of the amorphous material, carbon and minor content of apatite and anhydrite. The input fine grained material contained 1.6% CaO and 0.6% MgO. A new calcite-aragonite product was produced after one hour reaction at 22°C, 5 MPa and the stirrer rotation 300 rpm. This reaction time and conditions were used for all the experiments performed below. The calcite-aragonite had a crystalline structure and had a weight yield of 0.9% with 44 % of CaCO<sub>3</sub> (19 % CO<sub>2</sub> was bound in newly formed carbonate).

Slag, a by-product of cauldron burning of the black coal, represented by glassy material, was milled before carbonatization. The slag contained 99.7% of amorphous silicate material. The input material contained 2.4% CaO and 1.2% MgO. A new crystallized calcite-aragonite had a weight yield of 0.54% with 34 % CaCO<sub>3</sub> (15 % CO<sub>2</sub> was bound in newly formed carbonate).

During carbonatization of milled asbestos cement (eternit), the input fibroidal material contained 35% CaO and 5% MgO. As a result, 19% of CaO was bound into CaCO<sub>3</sub> including 16% of CaO in larnite (free for reaction), while MgO was bound into fibroidal chrysotile. After the crystallization the new calcite-aragonite product had a weight yield 2.3 % with 66 % of CaCO<sub>3</sub> (29 % CO<sub>2</sub> is bound in this carbonate).

Carbonatization of eternit was also made with prior mechanical-thermal reactivation. The input material contained 48 % CaO and 7 % MgO. After carbonatization 18 % of CaO was bound in CaCO<sub>3</sub> and 30 % of CaO was bound in bredigite. MgO was bound in mechanically-thermally activated chrysotile. A new crystallized calcite-aragonite product

had weight yield of 6% with a content of 14% of newly formed calcite-aragonite and 68 % hydromagnesite. Laboratory experiments have demonstrated that, at the above stated reaction conditions one tonne of CO<sub>2</sub> was bound to 28.8 tonnes of mechanically-thermally modified eternit. The poorer results from using eternit for CO<sub>2</sub> sequestration compared to ultramafic rocks were caused by the primary bounds of CaO in the eternit calcite structure. The methodology of artificial carbonatiza-

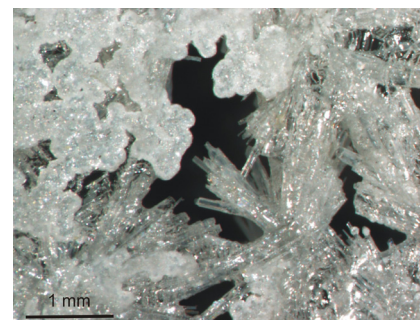


Fig. 5 Nesquehonite (needles on the lower right side) and hydromagnesite (spherical shape; the left upper side) represent carbonates produced after the reaction of CO<sub>2</sub> with ultramafic rocks

tion can significantly contribute to decreasing waste in dumps and can help neutralise the waste's alkalinity. In addition, this technique contributes towards the permanent removal of CO<sub>2</sub> from the atmosphere.

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