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

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

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

6. 1 Mineral carbonatization

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

In 2005, the method was finally defined in the IPCC Special Report on Carbon Dioxide Capture and Storage, part 7. Mineral carbonatization and Industrial uses of Carbon Dioxide (IPCC, 2005). According to this definition, mineral carbonatization is based on the reaction of CO_2 with oxides resulting in formation of insoluble carbonates. In the course of carbonatization CO_2 reacts with oxides of elements, such as for example Mg, Ca, or Fe, to form carbonates and at the same time heat develops at different levels according to the general equation (IPCC, 2005):

$$\mathbf{MO + CO_2 \rightarrow MCO_3 + heat\ (kJ.mol^{-1})} \quad (1),$$

according Bochenczyk et al. 2007:

$$\mathbf{CaO + CO_2 \rightarrow CaCO_3 + 179\ kJ.mol^{-1}} \quad (2),$$

$$\mathbf{MgO + CO_2 \rightarrow MgCO_3 + 118\ kJ.mol^{-1}} \quad (3).$$

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

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

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

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

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

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

6.2 Procedure and the methodology of technological research

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

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

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

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

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

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

In the scope of the technical work there was carried out thermal modification of specimens. In selected samples chemical modification was realized in order to activate or extract Ca, Mg, and Fe components from suitable mineral compounds (e.g. serpentine minerals) or from amorphous mass to accelerate the reactions with CO_2.

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

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

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

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

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

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

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

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

The homogeneous parts of the input specimens and output products after carbonatization or filtration and crystallisation by drying were identified by X-ray diffraction analysis, chemical analyses, and microanalyses to demon-

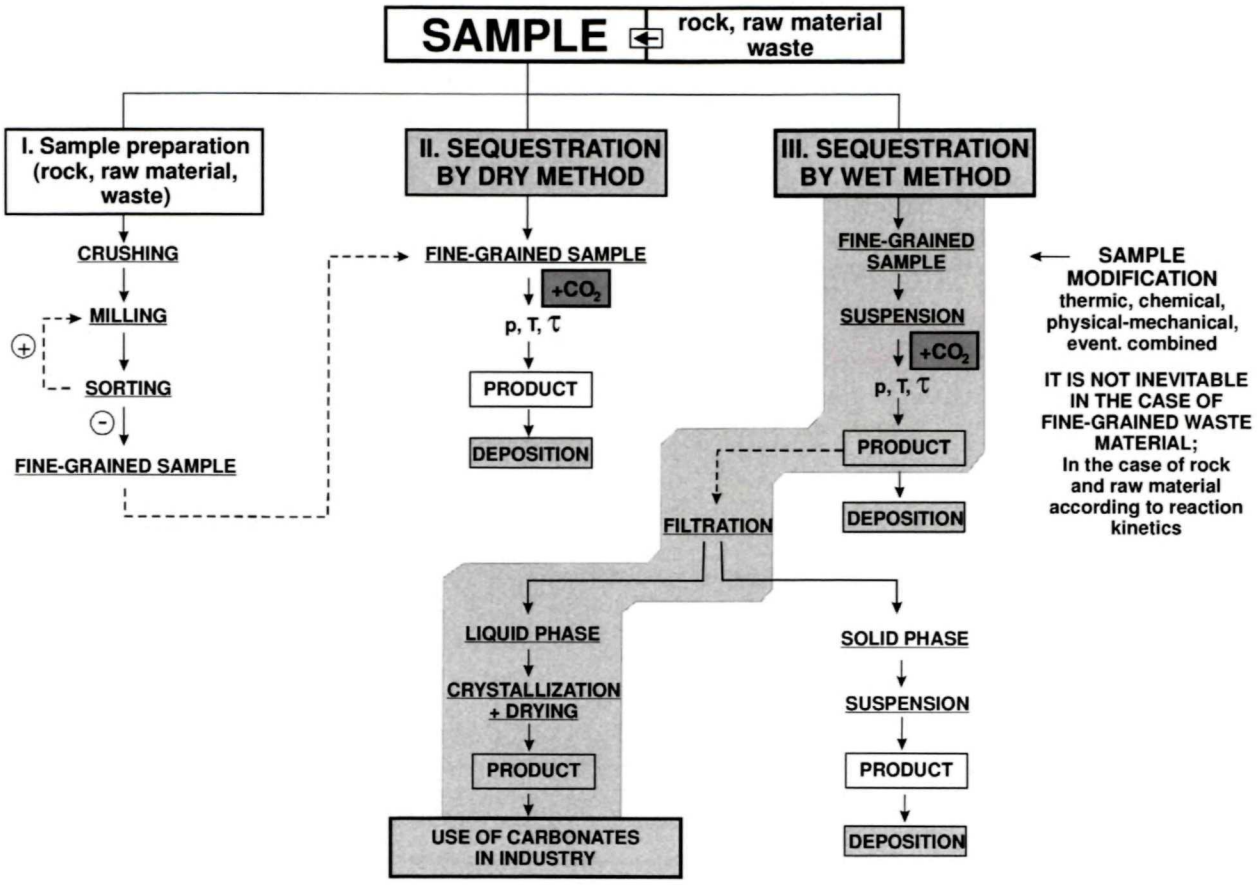


Fig. 6. 1 Scheme of research of samples carbonatization by CO_2 action

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

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

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

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

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

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

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

6.3 Characteristics of the input samples of geological materials

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

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

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

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

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

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

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

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

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

6.4 The results of experimental research of mineral carbonatization

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

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

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

6.4.1 Site Hodkovce - Serpentines

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

Tab. 6.1 Chemical composition of input samples

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

Note: Fe_2O_3 total content;

Tab. 6.2 Mineral composition of input samples

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

Note: tr. – traces (< 1%)

6.4.1.1 Laboratory tests of carbonatization using HO-2 sample material

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

Mechanical modification of the sample

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

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

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

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

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

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

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

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

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

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

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

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

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

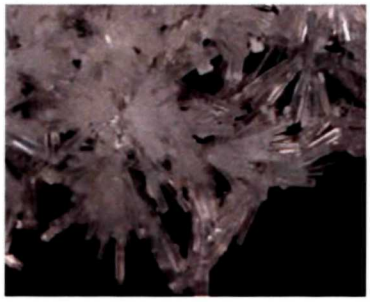
In the temperature range 360-460 °C it occurs the release of one molecule of water from the crystal lattice of nesquehonite. At the interval 460-580 °C the destruction of the crystal lattice occurred, with a loss of 31.3% of mass for the range of 360-580 °C (31.81% in theory).

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

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

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

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



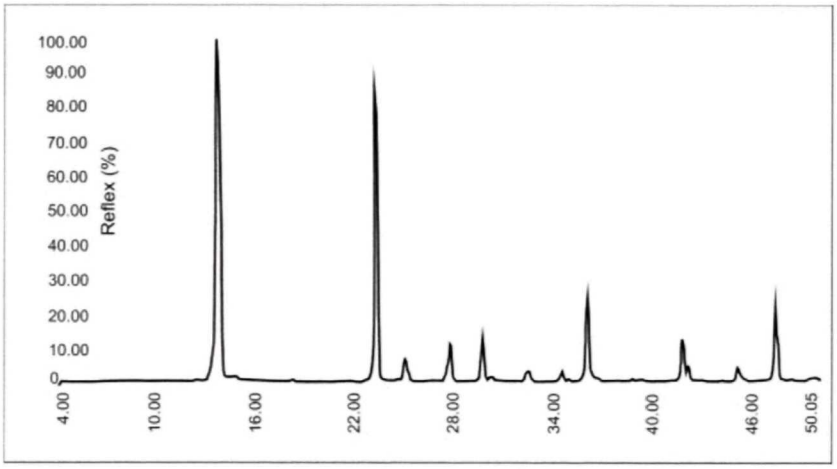


Fig. 6.2 X-ray diffraction record of the product precipitated from the filtrate (drying at 50 °C) with a dominant nesquehonite prepared by carbonatization from mechanically and thermally activated HO-2 sample

In the temperature range of 360-460 °C it occurred a release of OH functional group from the crystal lattice of hydromagnesite, while within the interval of 460-580 °C the disintegration of the crystal lattice occurred, with the release of CO_2 accompanied by a mass loss of 35.1 % for the range of 360-580 °C (in theory, 36.25 %).

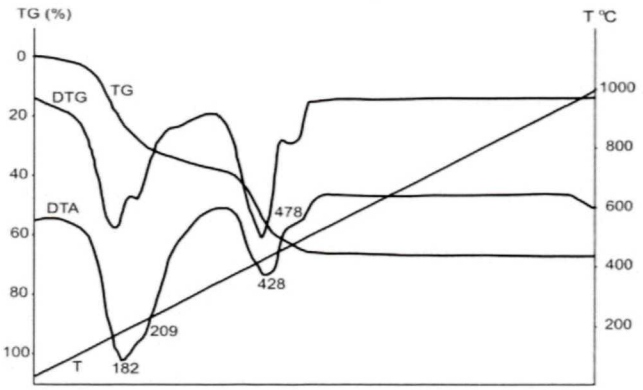


Fig. 6.3 Thermal analysis of the precipitated product from the filtrate (drying at 50 °C) with a dominant nesquehonite prepared by carbonatization from mechanically and thermally activated HO-2 sample

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

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

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

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

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

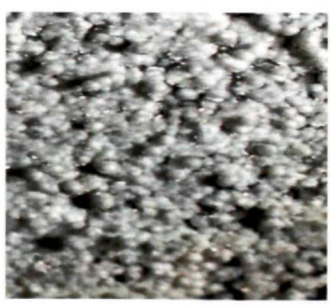
Hodkovce 2 – nesquehonite					
Number	Measured values			Table values	
	angle	d (nm)	I	d (nm)	I
1	13.750	0.644	100.00	0.648	100.00
2	23.210	0.383	85.57	0.385	75.00
3	24.940	0.357	7.23	0.359	8.00
4	27.670	0.322	11.61	0.323	20.00
5	29.600	0.302	13.34	0.303	30.00
6	30.140	0.296	1.97	0.298	6.00
7	32.340	0.277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

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

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

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

Compound	Product	% of compound content by weight					
		SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	CO_2
chemical	precipitated from filtrate	0.99	0.04	0.16	0.50	28.4	31.4
mineral		nesquehonite 97.5%; calcite 0.9%; oxides Si, Al,... 1.6%;					



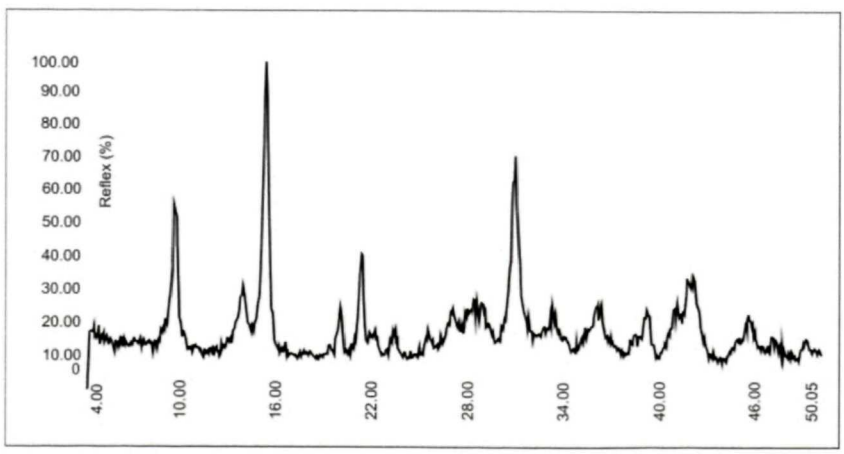


Fig. 6.4 X-ray diffraction record of the precipitated product from the filtrate (drying at 200 °C) with a dominant content of hydromagnesite prepared by carbonatization from mechanically and thermally activated HO-2 sample

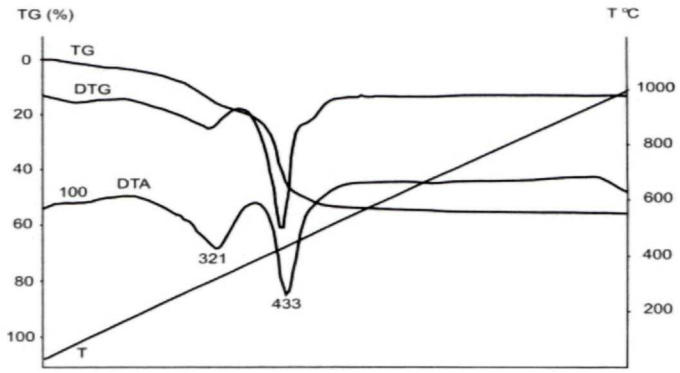


Fig. 6.5 Thermal analysis of the precipitated product from the filtrate (drying at 200 °C) with a dominant content of hydromagnesite prepared by carbonatization from mechanically and thermally activated HO-2 sample

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

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

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

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

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

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

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

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

Note: AF – amorphous phase

Thermal modification of sample

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

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

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

Note: AF – amorphous phase

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

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

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

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

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

Note: AF – amorphous phase

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

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

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

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

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

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

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

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

Note: AF – amorphous phase

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

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

Note: AF – amorphous phase

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

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

Note: AF – amorphous phase

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

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

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

Note: AF – amorphous phase

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

Chemical modification of the samples

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

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

carbonatization: $Mg(Cl)_2\ (l) + H_2O + CO_2\ (g) \rightarrow MgCO_3\ (s) + 2\ HCl\ (l)$ (5),

whereas the hydrochloric acid regenerates after carbonatization, or

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

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

carbonatization: $Mg(OH)_2\ (s) + CO_2\ (g) \rightarrow MgCO_3\ (s) + H_2O$ (8).

In the first case, the environment is strongly acidic (pH =1-2), and this two-stage "acid way" must meet strict technical requirements and instrumentation, and envi-

ronmental protection. In the latter case, the amount of sodium hydroxide neutralizes the excessive non-reacted hydrochloric acid with consequent formation of NaCl solution according to the equation: HCl + NaOH → NaCl + H_2O at pH = 6.5/7.5, while the magnesium hydroxide precipitate has to be washed and must be decanted from the substance, because in a subsequent step the CO_2 reacts with Na-ion preferably with the formation of undesirable sodium carbonates and thus contaminates the ultimate Mg-carbonate product.

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

A set of experiments was carried out only with the grit sample of HO-2 (Table 6.3), i.e., without mechanical modifications of grinding within the three-stage process (extraction - precipitation - carbonatization). In the first three experiments hydrochloric acid was used to extract Mg-component from the grit, in a period of 1, 2 and 3 hours at 22 °C, followed by precipitation, washing and decantation with subsequent carbonatization at a pressure of 6 MPa with CO_2 action of 1 hour at a temperature of 22 °C. In the other three experiments the conditions were the same, but with the extraction at 100 °C; the obtained results are shown in Table 6.18.

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

According to X-ray diffraction analysis even after three hours extraction at 22° C the filter cake contains a part of the intact lizardite. After the carbonatization of the precipitate in the high-pressure reactor for one hour at a CO_2 pressure of 6 MPa the newly created hydromagnesite products contained bound carbon dioxide from 10.3 to 14.7%, halite and iowaite, which binds Fe^{3+} in its structure.

According to the X-ray diffraction analysis patterns, after the extractions at 100 °C the filter cakes included also intact part of lizardite and amorphous substance. After the carbonatization of the precipitate at CO_2 input pressure of 6 MPa the precipitates included new hydromagnesite product binding carbon dioxide from 30.3 to 31.1%, i.e. the product containing approximately 80% of hydromagnesite and halite.

In order to avoid the process of precipitation in a three step process (extraction – precipitation – carbonatization) three experiments were carried out, in which the suspension of the HO-2 sample was directly exposed to 30% sodium hydroxide solution (extraction reagent) during 1, 2 and 3 hours at a temperature of 22 °C, followed by filtration, and the solid residue included the proportion of non-reacted lizardite and amorphous solid phase. In the reactor the filtrate (liquid phase) was exposed to carbon dioxide action for one hour at the CO_2 input pressure of 6 MPa and ambient temperature of 22 °C. The increments in the mass yield of the new products were high and ranged from 37.64% to 49.64% (preferential binding to Na-component from the added extraction reagent with CO_2), while according to the X-ray diffraction analysis the products included wegscheiderite and nahcolite (hydrocarbons and carbonates of sodium), brucite (magnesium hydroxide) and giorgiosite (magnesium carbonate).

The experiment with the sample of the modified grist (activated only during the three hours grinding) was carried out in two stages according to the "acid extraction method", whereas the suspension of the solid phase (grist samples): the liquid phase (water) = 10 g: 50 ml, was bathed in 20 ml of concentrated HCl. For one hour this mixture was mixed at 100 °C in rotary glass reactor for the purpose of extraction of the Mg-component and formation of magnesium chloride. After the extracting the suspension was filtered and divided to the filter cake containing amorphous phase + relics of lizardite, and the filtrate. The filtrate was subdued to CO_2 action with the input pressure of 6 MPa in the reactor during one hour (at room temperature). After carbonatization the product was dried at 200 °C, while the X-ray diffraction analysis found the presence of Mg-carbonates (hydromagnesite, dypingite, and giorgiosite) in addition to the non-reacting $MgCl_2.6\ H_2O$.

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

6.4.1.2 Mineral sequestration of CO_2 in HO-2 sample material

For the detection and determination of the dependence of reactivity of magnesium component from the serpentine of the HO-2 sample from Hodkovce site the carbonatization tests were carried out with only mechanically modified grist (grit ground for three hours – Table 6.4) with gradual increase of carbon dioxide action upon the suspension (1, 3, 6, 12 and 24 hours). The aim was to create the new Mg-carbonate product in the high-pressure reactor under optimal CO_2 input pressure of 6 MPa and ambient temperature 22 °C with stirrer speed 300 rpm. After the process the suspension was divided by filtration into the solid phase (filter cake) and the liquid phase (filtrate), from which the new product containing Mg-carbonate was obtained by drying-crystallization. The results of the laboratory experiments of mineral sequestration of CO_2 are shown in Table 6.19.

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

Chem. compound	Input **HO - 2**	Filt. cake after extr. at **22 °C**			Precipitated product after 1 h carbonatization		
		1 hour	**2** hours	**3** hours	**1** hour	**2** hours	**3** hours
MgO	36.73	25.7	22.8	21.6	26.8	27.2	28.5
CaO	0.24	0.14	0.16	0.20	0.39	0.27	0.21
Fe_2O_3	8.04	4.63	4.37	4.01	7.7	8.8	8.53
Loss by ign.	13.44	20.5	23.9	21.0	32.3	37.9	38.2
CO_2	0.19	0.43	0.74	0.54	10.3	14.7	13.0
Chem. compound	Input **HO - 2**	Filt. cake after extr. at **100 °C**			Precipitated product after 1 h carbonatization		
		1 hour	**2** hours	**3** hours	**1** hour	**2** hours	**3** hours
MgO	36.73	19.6	14.1	11.0	41.3	42.4	43.4
CaO	0.24	0.13	0.14	0.14	1.32	1.43	1.17
Fe_2O_3	8.04	4.4	4.53	3.8	0.03	0.03	0.04
Loss by ign.	13.44	16.3	16.4	16.6	51.9	51.7	52.0
CO_2	0.19	0.21	0.08	0.18	30.7	31.1	30.3

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

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

Note: AF – amorphous phase

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

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

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

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

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

The dependence of mass yield increment of the new precipitated carbonate product (y) upon the duration of CO_2 action (x), i.e. reactivity and binding of the Mg-component with the CO_2 within the crystal lattice of hydromagnesite in the grist of the sample HO-2 is characterised by the equation: $y = 0.229.Ln(x) + 0.7002$ with high correlation coefficient ($r = 0.9497$) at significance level 0.05 and for the selection range 5. According to this equation the increment in the mass yield of the new product in 6 days will be +1.84%, and, for example in 384 days + 2.79%, which testifies to the low speed of the reaction as a result of a insufficient release of the Mg-component from magnesium-rich minerals which underwent only mechanical modification with a duration of three hours.

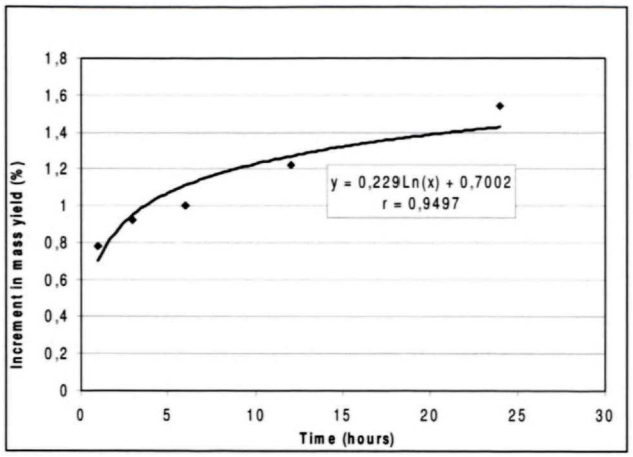


Fig. 6.6 Increments in the mass yield of precipitated products depending upon the time of CO_2 action upon mechanically activated HO-2 sample at CO_2 pressure of 6 MPa and ambient temperature 22 °C

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

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

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

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

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

Note: AF – amorphous phase

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

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

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

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

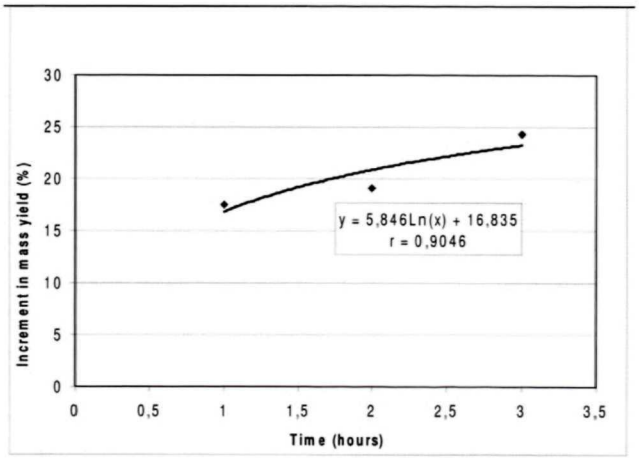


Fig. 6.7 Increments in the mass yield of precipitated products depending upon the time of CO_2 action upon mechanically and thermally activated HO-2 sample at CO_2 pressure of 6 MPa and ambient temperature 22 °C

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

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

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

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

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

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

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

6.4.1.3 Laboratory tests of carbonatization using HO-1 sample material

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

Mechanical modification of the sample

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

In the temperature range 360-460 °C the functional OH group was released from the crystal lattice of hydromagnesite with a mass loss of 22.1%, while in the range 460-580 °C the disintegration of the crystal lattice occurred, with the release of CO_2 and consequent mass loss of 12.3%, i.e. for a range of 360-580 °C the mass loss was 34.4% (theoretically 36.25%).

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

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

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

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

Note: AF – amorphous phase

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

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

Note: AF – amorphous phase

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

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

Thermal modification of the sample

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

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

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

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

Note: AF – amorphous phase

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

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

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

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

Note: AF – amorphous phase

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

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

Note: AF – amorphous phase

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

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

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

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

Note: AF – amorphous phase

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

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

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

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

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

The Table 6.32 shows that the proportion of Mg-component got in the reaction with CO_2 leading to the emergence of a new product containing hydromagnesite. However, from the Table 6.31, it is obvious that the increment in the mass yield of the new product with Mg-carbonate increased only slightly with CO_2 action duration - from the value of 0.78% (after 1 hour) to 1.58% (after 24 hours). This is due to the fact that via mechanical activation (grinding of the sample HO-1 for three hours on grain as referred to in Table 6.24) the Mg-component will still not be released sufficiently from the serpentine minerals for reaction with CO_2. This was attested by X-ray diffraction analysis, which detected presence of crystallic lizardite and olivine+pyroxene in the filter cake.

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

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

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

Note: AF – amorphous phase

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

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

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

Compound	Product	% of compound content by weight				
		SiO_2	Fe_2O_3	MgO	CO_2	Loss by ign.
chemical	**precipitated**	16.7	0,22	33,8	22,9	38,9
	filter cake	39.2	7,85	36,2	1,13	13,9
mineral	**precipitated**	hydromagnesite 60.8%; amorphous phase (+aragonite?) 39.2%;				
	filter cake	lizardite; maghemite; pyroxene+olivine;				

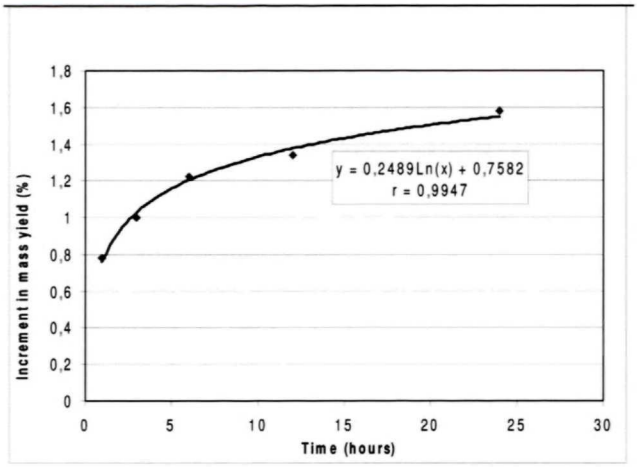


Fig. 6.8 Increments in the mass yield of precipitated products depending on the time of CO_2 action upon mechanically activated sample HO-1, at CO_2 pressure of 6 MPa and ambient temperature 22 °C

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

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

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

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

Note: AF – amorphous phase

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

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

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

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

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

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

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

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

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

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

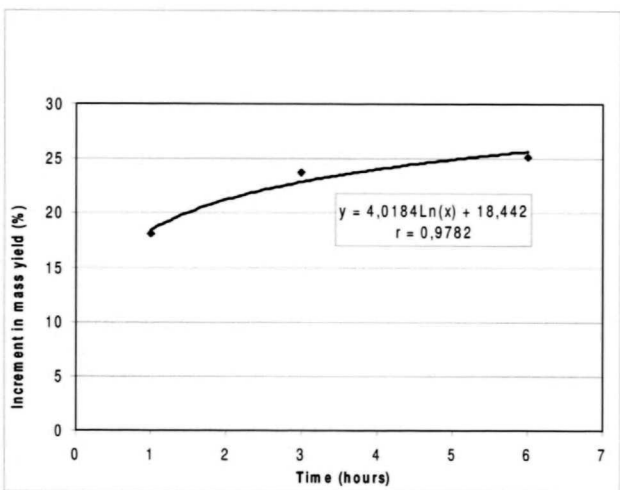


Fig. 6.9 Increments in the mass yield of precipitated products depending on the time of CO_2 action upon mechanically and thermally activated sample HO-1, at CO_2 pressure of 6 MPa and ambient temperature 22 °C

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

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

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

6.5 Overall assessment of the achieved results

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

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

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

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

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

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

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

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

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

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

- finer ground samples material is more suitable for the carbonatization;
- thermally modified sample material is more suitable;
- for the extraction of Mg-, or Ca-components from the entry material the temperature increasing and extending the duration of extraction is favoured;
- the efficiency of the extraction process is higher when using HCl than when using solution of NaOH;
- by drying the filtrate at 50 °C a new product precipitates with different content of nesquehonite depending upon the reaction conditions of carbonatization, or of extraction;
- by drying the filtrate at 200 °C a new product will precipitate with different content of hydromagnesite depending upon the reaction conditions of carbonatization, or of extraction;
- by drying the filtrate at 200 °C a new product will precipitate with different content calcite + aragonite depending upon the reaction conditions of carbonatization, or of extraction;
- dilution of suspension in water at carbonatization is manifested by lower crystallinity of hydromagnesite precipitated from the filtrate by drying at 200 °C;
- when using NaCl, or sodium hydroxide, in addition to the Mg-carbonates the precipitated product contained halite, Mg which can be removed by washing and decantation;
- at the extraction of Mg-component using HCl, in addition to the Mg-carbonates bischofite was present in the precipitated product (see chapter 7) and, the dominant were nesquehonite (drying at 50 °C), or hydromagnesite (drying 200 at °C) with a small content of amorphous substance and with the low contents of other Mg-carbonates (e.g. barringtonite, dypingite, giorgiosite, magnesite) documented by analysis using apparatus CAMECA SX 100, according to the reaction conditions.

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

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

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

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

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

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

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

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

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

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

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

The Table 6.36 shows that in the case of fully amorphous Mg-, or Ca-minerals in the entry samples grit milled sufficiently long, there occur a total destruction of the crystal lattice of the minerals. Thus full activation of the Mg- and Ca-components for reaction with CO_2 is achieved, i.e. full amount of Mg- and Ca-components tied to the minerals reacts with CO_2, forming $MgCO_3$ or $CaCO_3$, respectively (assumption of 100% conversion). 2.3 to 2.6 tonnes of a material from the serpentines samples are required to capture 1 tonne of CO_2, or 3.0 to 3.2 tonnes of material amphibolic-chloritic and talc serpentines samples per 1 tonne of CO_2, or from 5.6 to 14.4 tonnes of amphibolite and basalt samples material per 1 tonne of CO_2.

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

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

According to the values of the coefficient **k** in the equation the reactivity of the material samples is different. The highest reaction rate was achieved in serpentine samples designated **HO-1, HO-2 and RU-1**, in which the coefficient **k** ranged from 4.0 to 5.8 (HO-2), which is approx. 16 to 27 times the reaction rate against those samples only mechanically modified. In one hour carbonatization the new product with the increment in the mass yield ranged from 16.8 to nearly 22%. Paradoxically, the sample labelled **RU-2** from the same site (Rudník) had the reaction rate approximately 10 times lower (coefficient k = 0.5388 as opposed to 5.1263), but for one hour for both samples is the value of the increment in the mass yield of the new carbonate product similar (on average approximately 21.7%). Very good reactivity is manifested in the mechanically-thermally activated samples from the site Dobšiná (S-1) with a coefficient of 2.93 (grist) against coefficient 0.16 (ground grit); in this sample the highest value of the increment in the mass yield of the new product after one hour carbonatization was achieved up to 26.85% as opposed to the entry.

The reaction rate of the samples JA-1, KO-1/16 and BR-1 is expressed by the coefficient in the range 1.86-1.99, this means at least 10 x and higher, as in the samples only mechanically activated. A group of samples labelled KO-1/2, MI-1and FI-6 is characterised by the reactivity factor 0.82-0.98 (MI-1); in one hour the new carbonate product increment in the mass yield averages around 18.3% (KO-1/2 and MI-1) as compared to approximately 5 x less value (3.6% of sample FI-6).

In general, for the remaining group of mechanically-thermally activated samples (amphibolites and BE-1) the reactivity is low (~ 0.03 to 0,233) and comparable with the low coefficient of mechanically activated samples (~ 0.05 to 0.08), and after one hour of carbonatization at room temperature and CO_2 input pressure 6 MPa the increments in the mass yield of the new product containing Mg/Ca carbonates reached only from 0.29 to 4.3%.

Tab. 6.35 The contents of the granulometric classes (% by weight) in the samples grit and grist after 3 hours of grinding

Sample	Grit (mm)					Grist (mm)				
	+ 1.0	-1.0	+ 0.1	- 0.1	- 0.02	+ 1.0	-1.0	+ 0.1	-0.1	-0.02
HO-1	1.97	98.03	69.34	30.66	17.66	-	100.00	13.24	86.76	41.83
HO-2	2.13	97.87	73.96	26.04	17.47	-	100.00	7.27	92.73	46.32
RU-1	0.87	99.13	66.71	33.29	19.76	-	100.00	17.19	82.81	38.65
RU-2	2.67	97.33	73.26	26.74	13.70	-	100.00	20.30	79.70	39.97
JA-1	2.43	97.57	73.06	26.94	15.28	-	100.00	25.27	74.73	37.03
S-1	18.09	81.91	72.43	27.57	11.40	-	100.00	35.83	64.17	27.71
KO-1/2	76.46	23.54	92.93	7.07	-	0.68	99.32	72.07	27.93	11.12
KO-1/11	76.75	23.25	95.01	4.99	-	0.86	99.14	73.35	26.65	7.97
KO-1/16	75.16	24.84	90.81	9.19	-	1.32	98.68	70.29	29.71	10.28
BR-1	-	100.00	73.30	26.70	15.95	-	100.00	49.54	50.46	30.47
MI-1	-	100.00	59.44	40.56	23.82	-	100.00	41.70	58.30	32.50
FI-6	-	100.00	64.82	35.18	16.70	-	100.00	2.04	97.96	54.63
BE-1	-	100.00	70.24	29.76	15.34	-	100.00	5.07	94.93	52.54
ŠE-1	1.57	98.43	69.40	30.60	15.20	-	100.00	4.94	95.06	44.63
JK-1	-	100.00	76.96	23.04	10.17	-	100.00	40.05	59.95	30.03
BA-1	-	100.00	75.14	24.86	12.23	-	100.00	0.10	99.90	64.44
OS-1	-	100.00	75.07	24.93	14.60	-	100.00	0.40	99.60	69.13
BU-1	-	100.00	74.04	25.96	11.85	-	100.00	22.06	77.94	37.64

Tab. 6.36 The equations of the dependencies between the increments in the mass yields of the new carbonate product (y) of mechanically activated samples and the time of CO_2 action (x)

Sample	Equation	Correlation coefficient (r)	Significance level	Extent	**Quantity (t) of amorphous material /1 t CO_2**	
	y = k . Ln (x) + q				MgO to $MgCO_3$	MgO to hydromagn.
HO-1	y = 0.2489 . Ln(x) + 0.7582	0.9947	0.01; 0.05	5	2.540	3.174
HO-2	y = 0.2290 . Ln(x) + 0.7002	0.9497	0.05	5	2.493	3.116
RU-1	y = 0.1872 . Ln(x) + 1.8838	0.9414	0.05	5	2.635	3.294
RU-2	y = 0.2188 . Ln(x) + 1.1097	0.9881	0.01; 0.05	5	2.511	3.138
JA-1	y = 0.1942 . Ln(x) + 1.5798	0.9879	0.01; 0.05	5	2.527	3.159
S-1	y = 0.1603 . Ln(x) + 1.6418	0.9905	0.01; 0.05	5	2.538	3.171
KO-1/2	-	-	-	-	2.305	2.881
KO-1/11	-	-	-	-	2.370	2.962
KO-1/16	-	-	-	-	2.305	2.881
BR-1	y = 0.0715 . Ln(x) + 1.8096	0.9772	0.01; 0.05	5	2.482	3.102
MI-1	y = 0.1122 . Ln(x) + 1.5201	0.9881	0.01; 0.05	5	2.558	3.197
FI-6	y = 0.1087 . Ln(x) + 0.5821	0.9990	0.01; 0.05	5	3.046	3.806
BE-1	y = 0.0514 . Ln(x) + 1.1161	0.9899	0.01; 0.05	5	3.211	4.013
ŠE-1	y = 0.0549 . Ln(x) + 0.8341	0.8931	0.05	5	6.552*	7.376** (14.850 °)
JK-1	y = 0.0811 . Ln(x) + 1.0453	0.8729	0.05	5	6.675*	7.433** (13.612 °)
BA-1	-	-	-	-	7.816*	8.402** (12.007 °)
OS-1	-	-	-	-	14.361*	17.712** (265.111 °)
BU-1	y = 0.0625 . Ln(x) + 0.5730	0.9476	0.05	5	5.597*	6.284** (12.357 °)

The Table 6.37 in the seventh column presents the values of the quantities of thermally activated crushed material, and to the value the carbonatization duration is attached at the CO_2 input pressure of 6 MPa and ambient temperature. The values in the increments in the mass yield of the new carbonate product are less than 1%.

The Table 6.37 is amended on the Table 6.38, which presents the values of the increments in the mass yield of the new carbonate product activated mechanically-thermally for 1 and 6 hours (the results of laboratory experiments), and 6 and 384 days, respectively, calculated from the equations (Table 6.37), which were drawn up on the basis of the results of the experiments.

Tab. 6.37 The equations of the dependencies between the increments in the mass yields of the new carbonate product (s) from mechanically and thermally activated samples and the time of CO_2 action (x)

Sample	Equation	Correlation coeff. (r)	Significance level	Extent	Quantity (t) of mech. and therm act. rock /1 t CO_2		
	y = k . Ln (x) + q				MgO from serp.	Increment < 1%	CO_2/CH A/6 h.
HO-1	y = 4.0184 . Ln(x) + 18.4420	0.9782	0.05	3	4.086	8.511/24 hours	11.481
HO-2	y = 5.8460 . Ln(x) + 16.8350	0.9046	-	3	3.880	7.030/36 hours	12.109[1]
RU-1	y = 5.1263 . Ln(x) + 21.9540	0.9999	0.01; 0.05	3	5.069	6.743/30 hours	10.380
RU-2	y = 0.5388 . Ln(x) + 21.4010	0.9644	0.05	3	4.173	11.874/6 hours	12.907
JA-1	y = 1.9931 . Ln(x) + 13.2130	0.9978	0.05	3	4.346	14.616/12 hours	23.855
S-1	y = 2.9346 . Ln(x) + 26.8460	0.9892	0.05	3	3.599	7.518/18 hours	9.074
KO-1/2	y = 0.8591 . Ln(x) + 19.9790	1.0000	0.01; 0.05	3	4.520	12.343/6 hours	13.667
KO-1/11	-	-	-	-	-	-	-
KO-1/16	y = 1.9059 . Ln(x) + 16.1040	0.9237	-	3	4.343	12.745/12 hours	16.989
BR-1	y = 1.8597 . Ln(x) + 10.2020	0.9595	-	3	3.959	17.921/12 hours	26.385
MI-1	y = 0.9813 . Ln(x) + 16.6950	0.9658	0.05	3	3.717	14.397/6 hours	15.974
FI-6	y = 0.8204 . Ln(x) + 3.6029	0.9986	0.05	3	8.825	52.389/6 hours	83.333
BE-1	y = 0.0338 . Ln(x) + 4.3008	0.9982	0.05	3	7.641	57.985/6 hours	84.034
ŠE-1	y = 0.1418 . Ln(x) + 1.1300	0.9848	0.05	3	21.379	162.338/6 hours	248.880
JK-1	y = 0.0574 . Ln(x) + 1.0847	0.9793	0.05	3	15.215	190.985/6 hours	231.546
BA-1	y = 0.0760 . Ln(x) + 0.2934	0.9775	0.05	3	19.716	528.541/6 hours	961.538
OS-1	y = 0.2332 . Ln(x) + 1.6620	0.9262	-	3	297.371	109.266/6 hours	127.324
BU-1	-	-	-	-	-	-	-

The Table 6.38 shows that the most promising samples for carbonatization are the serpentines samples, and in particular the samples S-1 and RU-1, in which the increments in the mass yield of the new carbonate product were over 30% for 6 hours. Than followed the samples HO-1 and HO-2 (increment approx. 25-30%), samples RU-2, KO-1/2 and 1/16 (approx. 20-25%), JA-1 and MI-1 (approx. 15-20%) and BR-1 (increment approx. 10-15%). Other samples examined in view of the values of the increments in the mass yield are not promising for the fixation of CO_2.

6.6 Conclusions of the technological research

The most important output and the contribution of the technological research is identification and experimental demonstration of gaseous carbon dioxide sequestration in the geological materials from various sites across Slovakia in laboratory conditions. The CO_2 is permanently and stable fixed within the new carbonate products, containing, in particular, hydromagnesite, calcite and aragonite.

Comparing the groups of input samples has shown, that the samples of the first group-serpentines have clearly the highest sequestration potential, in which the content of magnesium component ranges from 34.75% to 39.73%. In second place are the samples of amphibolic-chloritic and talc serpentines, where the MgO content ranges from 30.07-33.50%. The samples from the groups of amphibolite and basalt reported in terms of the contents of MgO and free CaO (unbound to carbonates) have low sequestration potential.

Tab. 6.38 Increments in the mass yields of the new carbonate products of mechanically and thermally activated samples vs the time of CO_2 action

Sample	Increment in the mass yield of the new carbonate products (%)			
	From laboratory experiments		Calculated from equations in Table 6.37	
	1 hour	**6 hours**	**6 days**	**384 days**
HO-1	+ 18.10	+ 25.10	+ 38.41	+ 55.12
HO-2	+ 17.48	+ 24.36[1]	+ 45.89	+ 70.20
RU-1	+ 21.98	+ 31.18	+ 47.43	+ 68.75
RU-2	+ 21.46	+ 22.46	+ 24.08	+ 26.32
JA-1	+ 13.16	+ 16.70	+ 23.12	+ 31.41
S-1	+ 27.02	+ 32.38	+ 41.43	+ 53.64
KO-1/2	+ 19.98	+ 21.52	+ 24.25	+ 27.82
KO-1/11	-	-	-	-
KO-1/16	+ 16.42	+ 20.02	+ 25.58	+ 33.50
BR-1	+ 10.42	+ 13.88	+ 19.44	+ 27.18
MI-1	+ 16.80	+ 18.62	+ 21.57	+ 25.65
FI-6	+ 3.62	+ 5.10	+ 7.68	+ 11.09
BE-1	+ 4.30	+ 4.36	+ 4.47	+ 4.61
ŠE-1	+ 1.14	+ 1.40	+ 1.83	+ 2.42
JK-1	+ 1.08	+1.18	+ 1.37	+ 1.61
BA-1	+ 0.30	+ 0.44	+ 0.67	+ 0.99
OS-1	+ 1.70	+ 2.14	+ 2.82	+ 3.79
BU-1	-	-	-	-

According to the carbonatization results obtained the most perspective for CO_2 mineral sequestration is serpentine material with MgO-component content of about 37% tied mainly to serpentine minerals (chrysotile, lizardite), less to the minerals of olivine.

The best conclusive results, regarding the quality of prepared Mg-, or Ca-carbonates were achieved at CO_2 input pressure of 0.3 MPa, at carbonatization duration 1 hour at ambient temperature (22 °C) with the thermally activated samples (650 °C for 1 hour), in particular, from the serpentines group. By drying of the filtrate at 50 °C the new highly-pure product precipitated containing nesquehonite in the range 93.8-97.9% or hydromagnesite in the range 90.6-97.5%; at 200 °C drying of filtrates the dominant content was calcite+aragonite.

The simulation of P-T-t conditions of the carbonatization process and testing of CO_2 storage options in the newly created carbonate products with the subsequent finding and determination of magnesium, or calcium components reactivity of the input samples mechanically, or mechanically-thermally modified was carried out in the high-pressure stirring reactor PARR 4540. The optimum CO_2 input pressure was 6 MPa and ambient temperature was 22 °C. optimum stirrer speed 300 rpm. After the process the suspension was divided by filtration into the solid phase (filter cake) and the liquid phase (filtrate), from which the new product containing carbonates was obtained by drying-crystallization.

For the samples just mechanically, or both mechanical thermally activated the value of the increment in the mass yield of the new carbonate product (y) is the function of the natural logarithm of the carbonatization duration (x), i.e. $y = k.Ln(x) + q$, where q is the increment in the mass yield of the carbonate product after one hour.

According to the values of the coefficient **k** in each of the equations (Table 6.36) all the material just mechanically modified has low reactivity and reaction rate of Mg-, or Ca-components with CO_2 due insufficient release of Mg- or Ca-component from the entry minerals. In general, for the serpentines group of samples the reactivity is slightly higher ($k \sim 0.072$ to 0.249) than in the other samples ($k \sim 0.051$ to 0.109), and after one hour of carbonatization at room temperature and CO_2 input pressure 6 MPa for all samples the increment in the mass yield of the new product containing carbonates reached only up to +1.88%.

In the case of total amorphization of entry Mg- and Ca-minerals by sufficiently long grinding of the grit at estimated 100% conversion on $MgCO_3$, or $CaCO_3$, respectively, 2.3 to 2.6 tonnes of serpentines samples material are needed for fixation of 1 t of CO_2, from 3.0 to 3.2 tonnes of amphibolic-chloritic and talc serpentines samples material for fixation of 1 t of CO_2 or from 5.6 to 14.4 tonnes of amphibolite and basalt groups samples material for fixation of 1 t of CO_2 (Table 6.36).

In the case of 100% conversion of Mg-, or Ca-component on the hydromagnesite, or calcite+aragonite, 2.9 to 3.3 tonnes of serpentines samples material are required for fixation of 1 t of CO_2, from 3.8 to 4.0 of amphibolic-chloritic and talc serpentines samples material for 1 t of CO_2 or from 6.3 to 17.7 t of amphibolitee and basalt groups samples material for1 t of CO_2 (Table 6.36).

For the mechanically-thermally activated samples the highest reaction rate was achieved in serpentines HO-1, HO-2 (Hodkovce) and RU-1, in which the coefficient **k** ranged 4.0 to 5.8, which is approx. 16 to 27 times the rate of a reaction of those samples only mechanically modified. Thus, in one hour of carbonatization new product is formed with a the increment in the mass yield from 16.8 to nearly 22%.

In terms of the input materials for the carbonatization an entry raw materials should be cheap and the site should be located in the vicinity of the processing plant, or a producer of CO_2 emissions. Welcome are the input materials with mineral components present, which have an exothermic reaction with CO_2, i.e. the heat that develops in the reaction can be utilised for carbonatization. For example, in the case of serpentine in the reaction with CO_2 a heat of 349 $kJ.mol^{-1}$ CO_2 is released (exothermic reaction), in the case of forsterite in the carbonatization reaction 280 $kJ.\ mol^{-1}$ heat of CO_2 is being released (Seifritz, 1990).

The results of the experimental laboratory research will, at least, partially contribute to the definition of the reactivity parameters affecting the conversion of gaseous CO_2 within geological materials into harmless solid mineral component (carbonates), which in the future may be the source for the design of technological schemes (implementation projects) in the model, pilot and operational scale for enterprises, which will necessarily have to reduce CO_2 emissions.

Finally, the exploitation of research results of CO_2 sequestration (disposal) by the way of carbonatization may contribute in the future to the four positive facts:

1) reduction in the quantities of CO_2 emitted into the atmosphere;

2) the reduction in the quantities and changing the properties of the stored waste materials;

3) saving the raw material resources by preparation of products which may be used in the industry;

4) the protection and creation of the environment as a whole.