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Liquidation of CO_2 by carbonatization: Comparison of sequestration potentials of chromium-magnesium waste material and selected rock types

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Abstract

The artificial carbonatization of materials containing CaO, MgO or FeO (besides other oxides, non-reactive with CO_2) by reaction of their fine-grained grist with suspension of CO_2 plus water at appropriate reaction conditions (suspension density, pressure, duration of reaction, as well as the stirrer rotations) can contribute to stable liquidation of CO_2, as well as to liquidation of some environmentally harmful components from these materials, and optimizing of pH in the storage dumps.

The carbonatization results of until untested industrial waste – chromium-magnesium brick from the linings of furnaces (MT) are compared with the sequestration (carbonatization) potential of yet untested natural material – rocks with primary higher contents of CaO, MgO and FeO – the talc-chlorite schist from the locality of Gemerská Poloma (GP), metabasic rock from Nižný Klátov (NK1), chloritic schists from Gelnica (GE) and pyroxenic andesite from the quarry at the village of Slanec (SL). From practical reasons, the tested rock types occur in the nature in large quantities or are available as a by-product of already existing exploitation activities.

The waste sample MT has a high carbonatization potential – Mg component from the input reacted with CO_2 to hydromagnesite with a relatively high conversion – 83.2 %, and a new carbonate product with contents of 73.5 % of hydromagnesite and 1.1 % of $CaCO_3$ (together 74.6 %), can bound 28.2 % of CO_2. For liquidation of 1 tonne of CO_2 applying the grist of chromium-magnesium waste there is a need of 1.757 tonne of MT sample material, which represents even the better result than was obtained at previous researches applying serpentinite rock. Moreover, the positive fact is that the strongly alkaline reaction of input suspension of the sample MT (pH ~ 9.5 to 11.0) was lowered by the reaction to pH ~ 7.5.

Of the rock samples, the best carbonatization results were obtained at the talc-chlorite schist sample GP with the subsequent amorphization (GPA). A new carbonate product that has crystallized from the filtrate, has a content of 86.6 % hydromagnesite, in which structure 32.6 % CO_2 was fixed with an increase of the weight yield of the compound product +5.44 %. The second positive sample of metabasic rock NK1 allowed to prepare a new carbonate product with the $CaCO_3$ content 86.6 %, in which structure totally 38.1 % CO_2 was bound with an increase of the weight yield of compound product +1.3 %. The andesite SL has provided a new carbonate product with 71.1 % $CaCO_3$, having bound in its lattice 31.3 % of CO_2 with a weight yield of compound product +0.6 %. The worst carbonatization potential was found in the case of the chlorite schist sample GE, providing carbonate product with 41.4 % of manganocalcite (+kutnahorite) with bound 18.2 % of CO_2 and a weight yield of compound product +0.4 %.

Key words: CO_2 sequestration, carbonatization vs. carbonation, chromium-magnesium waste, talc-chlorite schist, metabasic rock, chlorite schists, pyroxenic andesite

Introduction

The amount of anthropogenic CO_2 emissions is constantly increasing. The total annual CO_2 flow from the soil and oceans into atmosphere is estimated to 500 billion tonnes. In 2011, from this amount, the anthropogenic emissions represented app. 25 billion tonnes (Němec, 2011). In 2013, the total CO_2 production related to the fossil fuel combustion reached 39.7 billion tonnes. Approximately 60 % of these emissions were produced by the large stationary sources like heating and power plants, steelworks and companies processing carbonatic raw materials. The emissions from these sources contain CO_2 dispersed in flue gases in the share of 5 to 15 % (Němec, 2011). By this reasons, from 2000 the amount of CO_2 in the atmosphere increases by 2 ppm annually, in 2007 there was reached the value 384 ppm (Sipilä et al., 2008). The 2013 average is 396.48 ppm. (www.CO_2Now.org).

The global temperature increase is interpreted by an increase of atmospheric CO_2 concentration. CO_2 is understood as a significant greenhouse gas, though also methane recently appears as an actual threat in relation to the shale gas exploitation.

It is estimated that maintaining an economic growth would increase the anthropogenic CO_2 emissions until 2030 by 70 % and in the 2070s the atmospheric concentration of CO_2 would achieve double value in comparison with the beginning of the last century (Němec, 2011).

European Commission has accepted a strategy to reduce CO_2 emissions in EU member states by 20 % until 2020. The strategy of the carbon capture and storage (CCS) is supposed as one of main ways how to reduce CO_2 emissions into the atmosphere. CCS includes the capture, separation and concentration of CO_2, being produced by the energy resources and industry, its transport to the storage sites and final storage protected against deliberation into atmosphere.

New investigation, reported in this article, was based on very positive results, reached in artificial carbonatization of ultramafic rocks – serpentinites (Tuček et al., 2008; Radvanec et al., 2008), but also an industrial waste – asbestos cement – eternit (Radvanec et al., 2013), as well as the fly ash (Tuček et al., 2011a, b).

The CaO, MgO and FeO components present in reacting substances are able to bound CO_2 at appropriate temperature-pressure reaction conditions (in the case of iron only as Fe^{2+}), and as the new products there originate carbonates and acid carbonates (calcite, aragonite, hydromagnesite, magnesite, dolomite, siderite, a.o.) with fixed CO_2 in their lattices.

The research (l.c.) has revealed that besides the temperature and pressure, the kinematics of CaO, MgO and FeO reaction with CO_2 resulting in origin of carbonates (the process of carbonatization, resp. artificial carbonatization) is influenced also by the mineral and chemical composition of input materials, activity of their compounds, purity of CO_2, state of input components (solid, liquid and gaseous phase) and their mutual ratio, grain-size, resp. porosity of input materials (waste or rocks), activity of specific surface, modification of input components (mechanical, thermic, chemical, physical--mechanical, event. their mutual combination), duration (lasting) of reaction with CO_2, reaction conditions (static or dynamic), density, resp. viscosity of reagent slurry, pH of reaction environment, type and amount of added reagents (additives). Hence, the effective carbonatization process needs an optimization of above listed parameters.

Authors explain the reasons of their using the term *artificial carbonatization* (related to the mineral carbonate) instead of frequently used term *carbonation* (derived from the chemical element carbon). The carbonatization is a process of material (mineral) transformation – the chemical reaction of an appropriate matter with carbon dioxide producing a new phase – carbonate in the form of synthetic minerals.

Based on recently solved geological project of the Ministry of Environment of the Slovak Republic "Determination of optimum conditions for permanent disposal of CO_2 by the method of mineral sequestration" (Čechovská et al., 2013), the carbonatization potential of until untested industrial waste – **chromium-magnesium material from the linings of furnaces (MT)** was investigated. During many years lasting industrial operation of furnaces the chromium-magnesium bricks were exposed to temperatures 1 650–1 750 °C.

In order to compare the sequestration (carbonatization) potential of this industrial waste with yet untested natural materials – rocks with primary increased contents of CaO, MgO and FeO – we have sampled the representative lithological types – **talc-chlorite schist from the locality of Gemerská Poloma (GP), metabasic rock from Nižný Klátov (NK1), chloritic schists from Gelnica (GE)** and **pyroxenic andesite from the quarry at the village of Slanec (SL).** From practical reasons, we intended to test rocks occurring in the nature in huge quantities and obtainable inexpensively, eventually being available as a by-product of already existing exploitation activities.

Samples and technique of laboratory investigation, analytical methods

Based on our previous experience (l.c.), we have defined four parameters, principally influencing carbonatization process – **duration of CO_2 reaction with appropriate suspension, concentration of suspension, CO_2 pressure during reaction, as well as stirrer rotations.** Other factors we have decided to remain constant in our optimization tests: mineral and chemical composition of input material and its solid phase, granular character of the sample obtained by its mechanical modification (crushing, milling, etc.), temperature of reaction environment is 20–22 °C (without the need of additional energy for heating the reaction), dynamic conditions of reaction, pH of environment (suspension) around 10, no need of adding other reagents than water for modification of input concentration of suspension. The CO_2 purity was at least 99 %, though in some cases we tested reaction products with CO_2 purity 95 %, and no worsening of results was revealed.

Tested sample of **chromium-magnesium material from the linings of furnaces (MT), as well as rock samples (GP, NK1, GE, SL),** had primary weight of ca 15 kg. Compact samples were crushed in jaw crushers, sorted and ground in ball mill to grain-size beneath 1 mm without residue. After their homogenization and quartering there followed wet granulometric analyses. Grist of investigated samples with differing granularity was then stirred in the water for suspension of appropriate parameters. Besides optimization of other parameters, the carbonatization tests in the reactor had to determine the optimum concentration of the particular sample mash.

The refinement and mechanical modification (activation) of the surfaces of grains of tested materials aimed to enlarge their specific reaction surface. Subsequent thermic, as well as chemical modifications have activated Ca, Mg, resp. Fe components from appropriate minerals in intention to accelerate their reactions with CO_2.

Laboratory experimental tests were done applying the laboratory high-pressure reactor PARR 4540. In tests presented in this contribution, the reactor parameters were as follows: CO_2 input pressures 2–12 MPa,

reaction durations 1–24 hours, stirrer rotation 250 to 550 rpm and suspension concentrates 80–370 g/l. The dynamic conditions of reaction with Mg, Ca, eventually Fe component from the input samples with CO_2 in water suspensions were provided by stirring. Found optimum stirrer rotation (400 rpm) changed only negligible due to the grain-size of given samples, their specific weight, etc.

Before carbonatization, the grist suspensions of input samples, especially that of waste material, have manifested strong alkaline reaction with pH 9.5–12.0. After reaction, the output pH values reached the range 6.5–8.0. The carbonatization products were obtained from the reactor either undivided, or divided by filtration to filtration cakes (solid phase) and filtrates (liquid phase). Drying at 100 to 200 °C has provided precipitated products with carbonate content for further analysing.

Both – the homogeneous parts of input samples, and products after carbonatization, resp. filtration and crystallization by drying, were identified by X-ray diffraction analyses, chemical analyses and some samples underwent also microprobe study for manifestation of CO_2 binding in solid products.

All chemical analyses of inputs and carbonatization products were performed in the State Geological Institute of Dionýz Štúr (SGIDS) – Geoanalytical Laboratories Spišská Nová Ves (GAL), representing the reference laboratories of the Ministry of Environment of the Slovak Republic for geology and analyses of geological materials with accreditation sensu ISO/IEC 17025:2005. The CO_2 contents were determined by the high-temperature oxidation and volumetric analysis (manometric method). CaO and MgO were determined by X-ray-fluorescence spectroscopy, FeO by titration analysis and loss by ignition by gravimetric method.

The semiquantitative and quantitative parameters of minerals in input samples and carbonatization products were obtained by the combination of X-ray diffraction (XRD) analyses and mineralogical recalculation from chemical analyses. The XRD analyses and all experimental procedures were done in the SGIDS laboratories – Applied Technology of Raw Minerals (ATNS, Košice): DRON – UM 1 having detection sensitivity 3 %: CoKα source, Fe filter, accelerating voltage 30 kV, amperage 20 mA, time constant T-2, apertures 2–2 and 1–0.25; shift of goniometer arm 2°/min. The computer processing of X-ray records by conventional ASTM tables has manifested the origin of qualitatively new mineral phases in the products.

Carbonatization products and filtration cakes were studied and documented applying binocular and optical microscope, as well as microprobe Cameca SX 100 in SGIDS Bratislava with following standards: Ca – wollastonite, Mn – rhodonite, Na – albite, K – orthoclase, Cr – chromite. Synthetic compounds were used for determination of Ti, Al, Fe and Mg contents, as well as BaF_2 for determination of F. Microprobe analyses were held at 15 kV accelerating voltage and beam intensity 5 nA at acid carbonates and carbonates analyses, or 20 nA at silicates and amorphous phases analyses. The silicates analysed area with the window diameter 1–7 μm changed according to analysed mineral or object dimensions. Acid carbonates and carbonates were analysed with the 7–20 μm window. The analysis duration for one element was 10 s or 25 s for F. The detection limit for individual elements was lower than 0.05 wt.% with an error ±1-sigma.

Tab. 1
Chemical and mineral composition of input samples MT, GP, NK1, GE and SL

	Jelšava	Gemerská Poloma	Nižný Klátov	Gelnica	Slanec
	MT	**GP**	**NK1**	**GE**	**SL**
	Waste	Rock samples			
Chemical composition (wt.%)					
SiO_2	1.43	51.70	52.10	56.70	58.20
TiO_2	0.03	1.16	1.05	0.90	0.69
Al_2O_3	3.88	12.70	14.90	22.90	18.80
Fe_2O_3	7.57	2.88	8.40	7.20	6.24
FeO	**0.43**	**1.90**	**5.82**	**4.46**	**2.80**
CaO	**2.09**	0.39	**6.33**	0.16	**7.71**
MgO	**78.30**	**22.40**	**7.57**	**1.59**	**2.73**
MnO	0.37	0.02	0.13	0.07	0.09
Na_2O	<0.20	<0.20	5.07	1.28	3.10
K_2O	0.06	0.59	0.11	4.76	0.91
P_2O_5	0.07	0.17	0.09	0.11	0.10
Cr_2O_3	5.66	0.0099	0.0296	0.0183	0.003
Loss ign.	0.37	7.74	4.03	4.09	1.00
SO_3	0.07	0.05	0.01	<0.01	0.31
CO_2	0.33	0.07	1.39	0.16	0.42
Mineral composition (wt.%)					
Brucite	1.2				
Portlandite					
Periclase	74.4				
Chromspinels	12.6				
Chrysotile					
Larnite					
Calcite	0.8		3.2	0.3	0.9
Plagioclase			42.9	10.8	61.8
Amphibole			31.5		
Maghemite	7.5				
Chlorite		47.7	21.1	16.6	
Talc		29.4			
Quartz		16.7		20.2	24.8
Sericite		6.2			
Mica				47.0	
K-feldspar				1.7	
Hydrocalumite					
Bassanite					
Other			1.3	3.4	6.2
Amorph. phase	3.5				6.3
Together	100.0	100.0	100.0	100.0	100.0

Note: Fe_2O_3 represents total content; other – Si, Al, Fe, ... oxides

Input samples for carbonatization – general information

Tested *waste sample* of the **chromium-magnesium material MT** represents the inner lining of furnaces of the Slovak Magnesite Works, joint-stock company, Jelšava.

Tested *rocks samples* encompass *(1)* the **talc-chlorite schist GP** from the mine dump at the village of Gemerská Poloma, *(2)* sample **NK1** of **metabasic rock** taken from the state road cut at Nižný Klátov ca 200 m to WNW from the crossing of the road to village. Sample *(3)* of **chlorite schist GE** sampled from the road cut 250 m to WSW of the railway station in the town of Gelnica. *(4)* **Pyroxene andesite SL** represents exploited rock in active quarry ca 500 m to NNE of the square in the Slanec village. All samples are from the Eastern Slovakia. Chemical and mineral compositions of input samples are presented in Tab. 1. Precise locations of the rocks sampling sites are presented in appropriate chapters and Figs. 5, 11a, 17a and 22a.

Mineral composition of input samples, as a precondition for effective carbonatization

As evident from chemical and mineral compositions in Tab. 1, the chromium-magnesium brick sample **MT** contains periclase (74.4 %), chromspinels (12.6 %) and brucite (1.2 %). From these minerals, as well as partly from amorphous phase (3.5 %), the Mg-, resp. Ca-components can be deliberated during carbonatization and react with CO_2. The sum of CaO, MgO and FeO in the case of sample MT is up to ca 81 %. Other minerals – maghemite (7.5 %) and calcite (0.8 %) do not react with CO_2.

Talc-chlorite schist sample **GP** (Tab. 1) contains 29.4 % of talc and 47.7 % of chlorite, being a significant bearer mainly of Mg and partly also of Fe^{2+}, both being appropriate for reaction with CO_2. Quartz (16.7 %) and white mica (6.2 %) have no CO_2 sequestering potential.

The metabasic rock sample **NK1** contains 31.5 % of amphibole with Ca, Mg and Fe^{2+} ions in its structure, next 21.1 % of chlorite, binding Mg and Fe^{2+}, as well as 42.9 % of plagioclase (source of Ca component; Tab. 1). All these minerals are appropriate for reaction with CO_2. Next minerals of rock – calcite (3.2 %) and Si, Al, Fe oxides (1.3 %) were not involved into carbonatization process.

Sample of chloritic schist **GE** contains only one mineral (chlorite 16.6 %), having bound in its structure Mg and Fe^{2+} ions, appropriate for binding CO_2. Further present minerals (Tab. 1) do not bind appropriate ions for reaction with CO_2, including plagioclase, having in its structure only Na – albite component (missing Ca).

In the pyroxenic andesite sample **SL** (Tab. 1), Ca, Mg and Fe^{2+} are available in plagioclase (61.8 %), amorphous phase of non-stoichiometric composition (6.3 %) and further minerals (6.2 %). Quartz (24.8 %) and calcite (0.9 %) are not appropriate for artificial carbonatization.

In the case of rock samples, the sum of Ca, Mg and Fe^{2+} oxides is in the range from ca 6 % (GE) up to ca 25 % (GP). The highest value of these three oxides is in the sample GP – 22.4 % MgO. Next there follow the samples SL – 7.71 % CaO, NK1 – 7.57 %, MgO and GE – 4.46 % FeO (Tab. 1). Mg is bound preferably in talc (GP) and chlorite (GP, NK1, GE). Ca component is present preferably in the structure of plagioclase (NK1, SL) and Fe^{2+}, resp. Ca components are present preferably in the structure of amphibole (NK1).

Results of carbonatization

Carbonatization of chromium-magnesium waste material (sample MT)

Carbonatization tests of the MT sample grist with the grain-size <1 mm

Grist of the input sample **MT** with the **grain-size <1 mm and 4.4 % of classy component <0 μm** (Fig. 1a, b) contains dominant periclase, less brucite and chromspinels, altogether reaching 74.4 % of MgO.

The reaction of the periclase and portlandite from the **chromium-magnesium waste** with the mixture $H_2O + CO_2$ takes place according to reaction (1).

Table 2 shows that the weight yields after carbonatization of the MT sample grist <1 mm gradually increased during the reactions lasting from one to six hours from +3.80 % up to +13.22 % and from six to eight hours the value has increased by ca 2 %. The highest weight yield was reached after **8 hours** of carbonatization (+15.4 %). An increase of CO_2 pressures (from 6 up to 12 MPa) in other separate successive reactions lasting 6 hours have produced approximately similar increase of the weight yield of undivided products of carbonatization – around 13 %. The products contained newly originated hydromagnesite, though the persisting presence of input Mg minerals was still confirmed by the XRD analysis.

Table 4 presents the results of artificial carbonatizations of **MT** sample grist, applying grain-size **<1 mm** at differing stirrer rotations. The final carbonatization products were divided by filtration to filtration cakes (solid phase – K) and filtrates (liquid phase – F), which were subsequently dried and carbonates containing products have precipitated. The highest weight yield (K + F) **+9.44 wt.%** was reached after **4 hours of reaction at 6 MPa** at stirrer rotations **400 rpm.** The hydromagnesite contents in products from filtrates are up to **89 %.**

The weight yields obtained after carbonatization of the MT grist with grain size <1 mm are low (ca 10-x lower than theoretical weight yield), filtration cakes still contain a lot of periclase and brucite and there is obvious that further milling is necessary for increasing of the reaction surface.

Figure 2 shows the micro composition of input MT chromium-magnesium waste as well as the product after its 4 hours lasting carbonatization. Chemical classification of calcite, dolomite and magnesite, originating by carbonatization of chromium-magnesium waste is presented in Fig. 3.

6MPa, 22 °C, 2 hours

$$\underset{\text{periclase}}{6MgO} + \underset{\text{portlandite}}{Ca(OH)_2} + 6CO_2 + 4H_2O \rightarrow \underset{\text{hydromagnesite}}{Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O} + \underset{\text{calcite-dolomite-magnesite}}{CaCO_3 + MgCO_3} \quad (1)$$

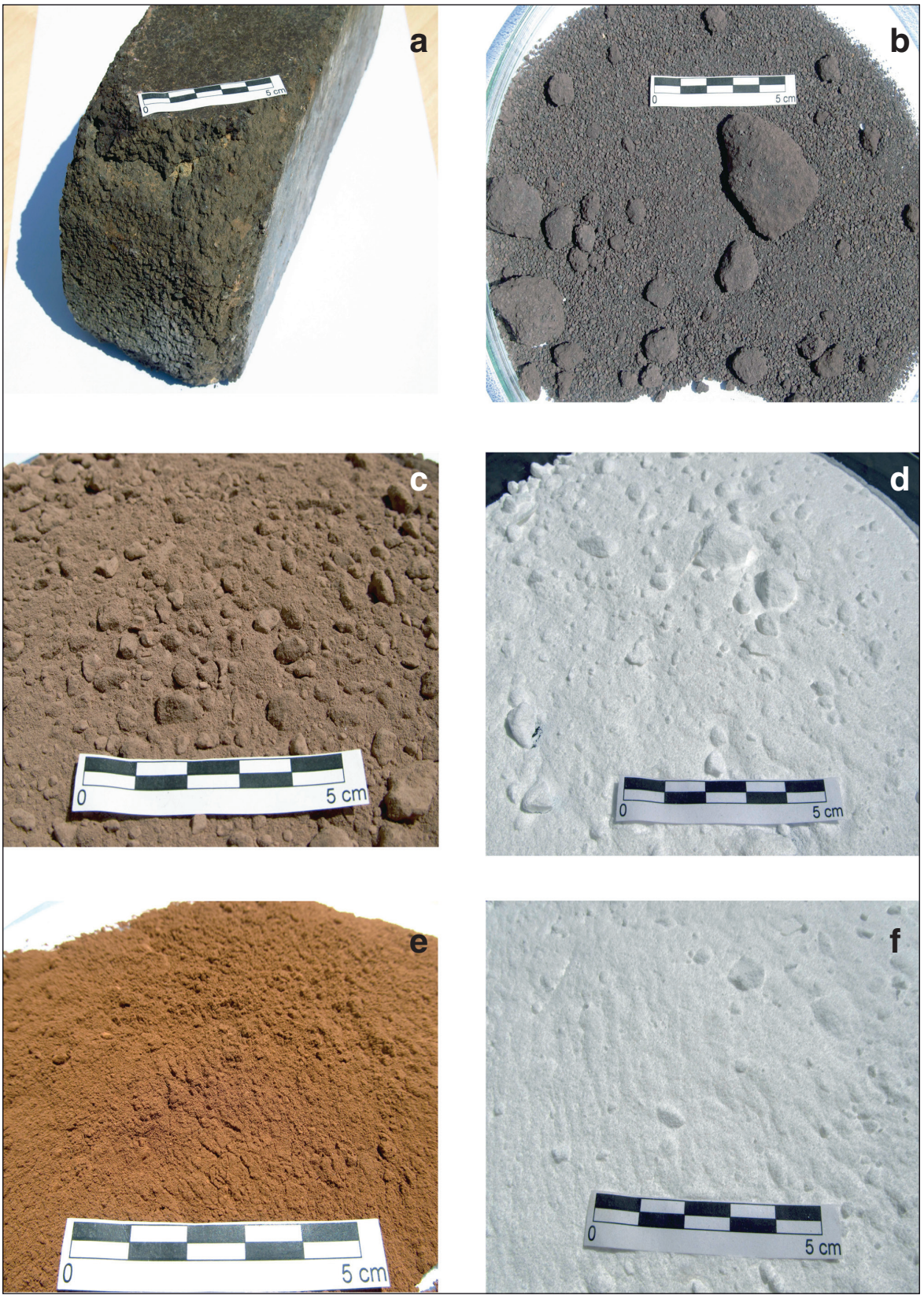

Fig. 1. a – Input sample of the waste chromium-magnesium brick MT. **b** – Grist of MT sample with a grain-size beneath 1 mm. **c–d** – Carbonatization products of the sample MT – filtration cake (c) and filtrate (d). **e–f** – Products of double carbonatization – filtration cake (e) and filtrate (f).

Tab. 2
Minerals and weight yields (%) in carbonatized products of the chromium-magnesium waste sample **MT** – fraction **<1 mm,** density **159 g/l,** temperature **22 °C,** stirrer rotation **400 rpm** in relation on **changed reaction duration (1–8 hours),** as well as **changed CO_2 pressures (6, 8, 10 and 12 MPa)** in reactions lasting **6 hours**

Duration of reaction with CO_2 (hours)	Weight yield (%)	Minerals in carbonatized product
Input	–	Periclase, brucite, calcite, maghemite, chromspinelides, AF
1	+3.80	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
2	+5.44	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
3	+7.58	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
4	+9.02	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
5	+10.12	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
6	+13.22	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
7	+13.54	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
8	+15.40	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
Pressure CO_2 (MPa)	Increase of weight yield (%)	Minerals in carbonatized product
Input	–	Periclase, brucite, calcite, maghemite, chromspinelids, AF
6	+13.22	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
8	+12.82	Periclase, brucite, hydromagnesite, calcite, maghemite, AF
10	+13.76	Periclase brucite, hydromagnesite, calcite, maghemite, AF
12	+12.48	Periclase, brucite, hydromagnesite, calcite, maghemite, AF

Note: AF – amorphous phase, containing in carbonatized products also chromspinels

Tab. 3
Wet granulometric analysis of the **MT** sample grists <0.2 mm and <0.1 mm

Grain size (mm)	**MT – Grist beneath 0.2 mm – Weight yield (%)**		
	Class	Total residue	Total throughs
0.2–0.5	–	–	–
0.1–0.2	9.73	9.73	–
0.063–0.1	15.43	25.16	90.27
0.045–0.063	10.63	35.79	74.84
0.020–0.045	24.44	60.23	64.21
–0.020	39.77	–	**39.77**
Sum	100.00	–	–

Grain size (mm)	**MT – Grist beneath 0.1 mm – Weight yield (%)**		
	Class	Total residue	Total throughs
0.1–0.2	–	–	–
0.063–0.1	5.00	5.00	–
0.045–0.063	10.70	15.70	95.00
0.020–0.045	29.80	45.50	84.30
–0.020	**54.50**	–	**54.50**
Sum	100.00	–	–

Tab. 4
The **MT** sample carbonatization tests applying fraction <1 mm at reaction conditions: **22 °C, 4 hours,** pressure **6 MPa,** suspension density **159 g/l** and **differing stirrer rotation**

Stirrer rotation (rpm.)	Product	Total increase of weight yield (%)	Chemical composition (wt.%)					Mineral composition (wt.%)
			Fe_2O_3	CaO	MgO	Loss by ign.	CO_2	PE – periclase; BR – brucite; HM – hydromagnesite; KA – calcite; Magh – maghemite; AF – amorphous phase
MT	Input	–	7.57	2.09	78.3	0.37	0.33	PE 74.4; BR 1.2; KA 0.8; Chrs 12.6; Magh 7.5; AF 3.5
350	Cake – K	+8.76	8.39	1.10	75.5	1.41	0.73	PE 74.0; BR 2.2; KA 1.7; Magh 8.4; next minerals 13.7
	Filtrate – F		–	6.51	39.5	51.3	33.9	Hydromagnesite 90.0; AF 10.0
400	Cake – K	**+9.44**	8.35	1.04	75.8	1.57	0.73	PE 73.9; BR 2.7; KA 1.7; Magh 8.4; next minerals 13.3
	Filtrate – F		–	6.05	39.4	52.0	33.7	Hydromagnesite 89.5; AF 10.5
450	Cake – K	+8.08	8.28	0.96	75.4	1.59	0.59	PE 73.2; BR 3.2; KA 1.3; Magh 8.3; next minerals 14.0
	Filtrate – F		–	5.74	40.6	51.6	33.8	Hydromagnesite 89.8; AF 10.2
500	Cake – K	+8.00	8.40	1.00	76.0	1.59	0.54	PE 73.7; BR 3.4; KA 1.2; Magh 8.4; next minerals 13.3
	Filtrate – F		–	6.18	39.9	51.5	33.1	Hydromagnesite 87.9; AF 12.1

Note: Chrs – chromspinels. In all cakes (K), the present chromspinels are included into the group of further minerals.

Carbonatization tests of the MT sample grist – grain-size <0.2 mm

Totally 90 minutes milling of the homogeneous part of the sample MT with grain-size <1 mm to grain-size <0.2 mm resulted in increased of the finest class (<20 μm) by 35.37 % to 39.77 % (Tab. 3).

The conditions of CO_2 reactivity with MgO were optimized in the high-pressure reactor with the MT sample grist <0.2 mm successively at eight reaction durations (1, 2, 3, 4, 5, 6, 7 and 8 hours), five CO_2 pressures (4, 5, 6, 7 and 8 MPa), three suspension concentrations (81, 159 and 215 g/l) and five stirrer rotations (350, 400, 450, 500 and 550 rpm) (Tab. 5). In the case of reacting the whole share of MgO (78.3 %) from Mg-bearing input minerals, resulting to crystallization of hydromagnesite, the maximum theoretical weight increase of undivided product after the reaction with CO_2 would represent an increase +103.4 %, i.e. from 1 kg of the input sample there would originate 2.034 kg of carbonatized product. The reaction tests intended to reach this maximum weight yield, i.e. no former Mg minerals periclase, brucite, resp. chromspinels should remain, or remain in the smallest possible amount.

The weight yields of compound products after carbonatization have continually increased by longer durations (Tab. 5) from one to four hours (from +27.28 % to +49.56 %), but reactions lasting five and six hours increased this value only by 1.44 %. The highest weight yield was reached after 6 hours (+51.0 %). Hydromagnesite was demonstrated by XRD in carbonatization products of all reactions, though periclase and brucite still remained in filtration cakes.

Increasing CO_2 pressure (from 4 to 6 MPa) in reactions caused an increase of the weight yield of compound product from +35.32 % to +49.56 %, though at pressures from 6 to 8 MPa it was approximately corresponding – around +49 %. Carbonatization products contain hydromagnesite, though Mg minerals (periclase, brucite) in filtration cakes were still found by XRD analysis.

Tests with various densities of suspensions have demonstrated that the highest total weight yield of compound carbonatization product +52.32 % was found at density 159 g/l. In filtration cakes the increased suspension density was reflected with lowering content of periclase from 58.6 % to 21.5 % and distinct increase of hydromagnesite from 2.4 % to 54.5 %. The precipitated products from filtrates contained 93.2–96.7 % of hydromagnesite.

Concerning the stirrer rotations (Tab. 5), the highest weight yield of compound product was reached at 400 rpm (+54.4 %) with the hydromagnesite content in dried product from filtrate was 97.5 %. The periclase content in filtration cake in comparison with the input (74.4 %) has lowered more than twice to value 35.9 %.

Because in all filtration cakes of this tests series with the grist of the grain-size <0.2 mm, the unreacted periclase and brucite still remained (Tab. 5) and the utmost reached weight yield of compound carbonatized product was +54.4 % (theoretically possible could be +103.4 %), there is necessary to test the above stated carbonatization parameters with even finer grist – the grain-size <0.1 mm. (At the grain-size <0.2 mm the class <1 mm represented only +15.43 % – Tab. 3).

Carbonatization tests of the MT sample grist with the grain-size <0.1 mm

Homogeneous part of the sample **MT** (<0.2 mm) was further milled 30 minutes to grain-size <0.1 mm. The representation of the finest class (<20 μm) has increased by 14.73 % to 54.50 % (Tab. 3).

Optimization tests of CO_2 reactivity with dominant MgO component from the grist of grain-size <0.1 mm were held in the high-pressure reactor with the same parameters combinations as in the first tests series – duration of reactions with **CO_2:** 1, 2, 3, 4, 5 and 6 hours, **CO_2 pressures:** 4, 5, 6, 7, 8 and 10 MPa and **suspension densities:** 81, 159 and 234 g/l (Tab. 6). Stirrer rotations were fixed at 400 rpm.

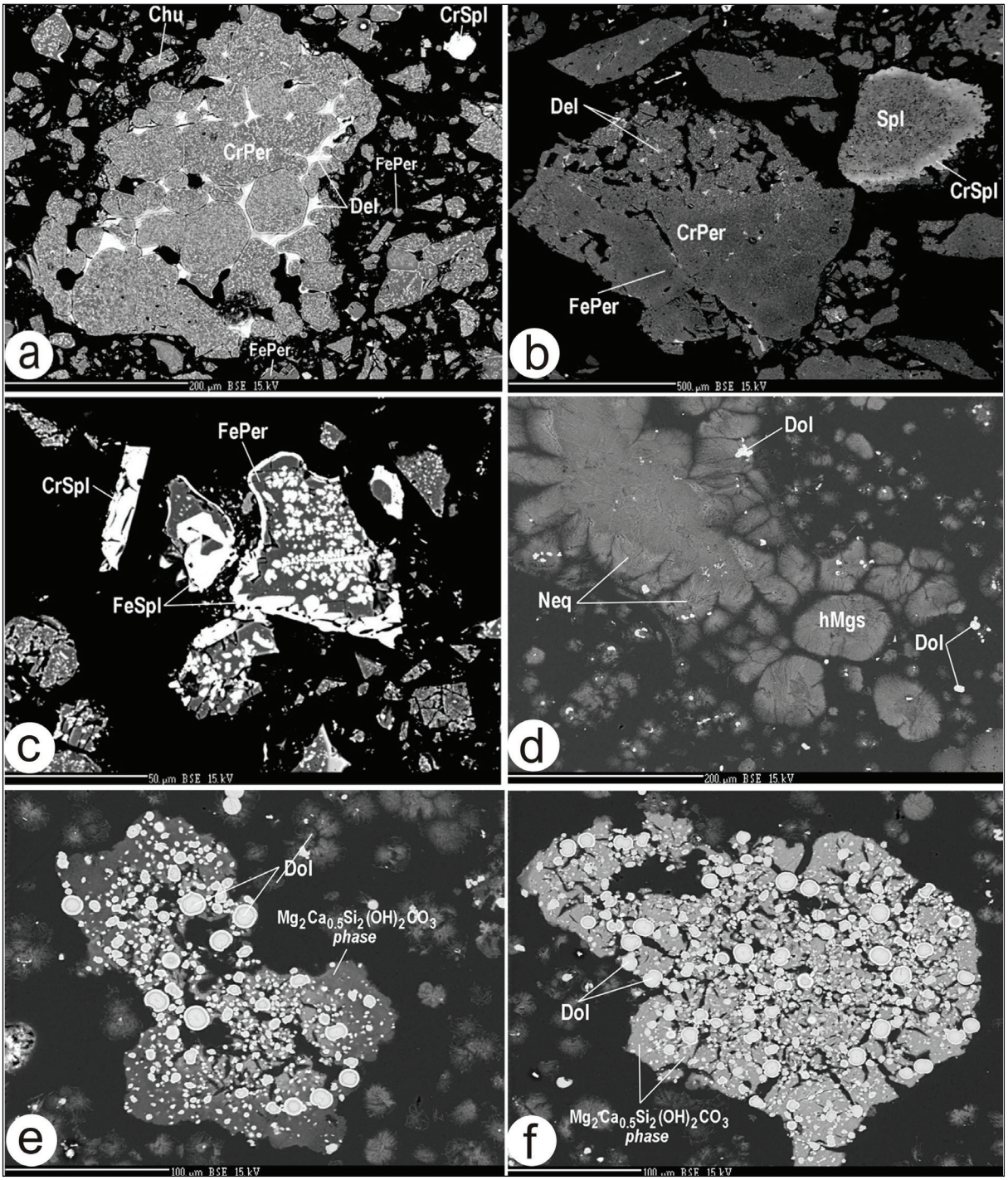

Fig. 2. Composition of the input **MT** chromium-magnesium waste (a–c) and the product (filtrate) after its carbonatization (d–f; 4 hours reaction). CrPer – Cr periclase; Chu – clinohumite; FePer – Fe periclase; CrSpl – Cr spinel; Spl – spinel; FeSpl – Fe spinel; Del – dellaite; Cal – calcite; Dol – dolomite; hMgs – hydromagnesite; Bar – barringtonite; Ser – serveegite; MgSer – Mg serveegite. BSE image.

Tab. 5
Results of the **MT** sample carbonatization tests – chemical and mineral compositions in cakes and filtrates (wt.%) – applying fraction **<0.2 mm,** reaction temperature **22 °C** at sequentially changed reaction pressure, suspension density, stirrer rotation and duration of reaction with CO_2

Changed reaction parameter	Product	Total yield (wt.%)	Chemical composition (wt.%)					Mineral composition (wt.%)
			Fe_2O_3	CaO	MgO	Loss by ign.	CO_2	PE – periclase; BR – brucite; HM – hydromagnesite; KA – calcite; Magh – maghemite; AF – amorphous phase
MT	Input	–	7.57	2.09	78.3	0.37	0.33	PE 74.4; BR 1.2; KA 0.8; Chrs 12.6; Magh 7.5; AF 3.5
Changed duration of reaction (1–6 hours) at pressure 6 MPa, suspension density 159 g/l and stirrer rotation 400 rpm								
1	Cake – K	+27.28	9.55	1.43	66.4	9.20	3.40	PE 53.4; BR 15.0; HM 6.1; KA 2.6; Magh 9.6; OM 13.3
	Filtrate – F		–	1.98	42.9	55.9	37.5	Hydromagnesite 95.5; AF 4.5
2	Cake – K	+ 34.70	9.88	1.56	65.0	9.59	4.19	PE 52.9; BR 12.6; HM 7.9; KA 2.8; Magh 9.9; OM 13.9
	Filtrate – F		–	1.18	43.6	56.0	37.3	Hydromagnesite 96.6; AF 3.4
3	Cake – K	+ 44.78	10.40	1.86	58.0	15.6	8.38	PE 41.9; BR 11.9; HM 18.4; KA 3.3; Magh 10.4; OM 14.1
	Filtrate – F		–	0.69	43.5	56.1	37.3	Hydromagnesite 97.6; AF 2.4
4	Cake – K	+ 49.56	10.00	1.78	55.9	19.0	10.9	PE 37.8; BR 10.5; HM 25.2; KA 3.2; Magh 10.0; OM 13.3
	Filtrate – F		–	0.75	43.6	57.5	38.2	Hydromagnesite 99.8; AF 0.2
5	Cake – K	+ 50.88	8.98	1.58	54.1	23.1	14.5	PE 34.9; BR 5.9; HM 35.2; KA 2.8; Magh 9.0; OM 12.2
	Filtrate – F		–	0.89	43.8	57.0	37.9	Hydromagnesite 98.8; AF 1.2
6	Cake – K	+ 51.00	10.80	1.96	56.4	16.2	9.54	PE 41.5; BR 8.3; HM 21.2; KA 3.5; Magh 10.8; OM 14.7
	Filtrate – F		–	0.63	43.4	56.8	37.7	Hydromagnesite 98.8; AF 1.2
Changed CO_2 pressures (4–8 MPa) at 4 hour reaction, stirrer rotation 400 rpm and suspension density 159 g/l								
4	Cake – K	+35.32	9.85	1.55	63.1	11.5	5.63	PE 50.0; BR 11.7; HM 11.7; KA 2.8; Magh 9.9; OM 13.9
	Filtrate – F		–	1.31	43.5	54.9	36.6	Hydromagnesite 94.5; AF 5.5
5	Cake – K	+ 37.82	10.40	1.82	65.6	11.1	5.46	PE 53.0; BR 11.6; HM 10.7; KA 3.3; Magh 10.4; OM 11.0
	Filtrate – F		–	0.84	43.7	56.4	37.5	Hydromagnesite 97.8; AF 2.2
6	Cake – K	+ 49.56	10.00	1.78	55.9	19.0	10.9	PE 37.8; BR 10.5; HM 25.2; KA 3.2; Magh 10.0; OM 13.3
	Filtrate – F		–	0.75	43.6	57.5	38.2	Hydromagnesite 99.8; AF 0.2
7	Cake – K	+ 48.54	10.00	1.52	61.4	13.6	7.83	PE 48.6; BR 7.7; HM 17.6; KA 2.7; Magh 10.0; OM 13.4
	Filtrate – F		–	1.32	43.3	56.0	37.4	Hydromagnesite 96.6; AF 3.4
8	Cake – K	+ 48.38	10.30	1.49	64.7	9.31	4.02	PE 52.9; BR 12.4; HM 7.6; KA 2.7; Magh 10.3; OM 14.1
	Filtrate – F		–	1.27	43.1	56.2	37.5	Hydromagnesite 96.9; AF 3.1;
Changed suspension density (81, 159 and 215 g/l) at 4 hour reaction, CO_2 pressure 6 MPa and stirrer rotation 400 rpm								
81	Cake – K	+39.88	10.10	0.93	69.0	6.31	1.64	PE 58.6; BR 13.6; HM 2.4; KA 1.7; Magh 10.1; OM 13.6
	Filtrate – F		–	2.63	42.4	53.3	35.1	Hydromagnesite 93.2; AF 6.8
159	Cake – K	+52.32	9.48	1.55	54.8	21.3	13.7	PE 37.8; BR 3.9; HM 33.2; KA 2.8; Magh 9.5; OM 12.8
	Filtrate – F		–	0.89	43.7	55.1	36.4	Hydromagnesite 96.7; AF 3.3
215	Cake – K	+48.59	6.22	1.10	50.1	34.2	21.4	PE 21.5; BR 7.5; HM 54.5; KA 2.0; Magh 6.2; OM 8.3
	Filtrate – F		–	3.39	42.1	54.2	35.8	Hydromagnesite 95.1; AF 4.9
Changed stirrer rotation (350, 400, 450, 500 and 550 rpm) at 4 hour reaction, CO_2 pressure 6 MPa and suspension density 159 g/l								
350	Cake – K	+48.08	8.98	1.87	56.5	19.7	12.6	PE 40.6; BR 4.5; HM 29.6; KA 3.3; Magh 9.0; OM 13.0
	Filtrate – F		–	1.06	43.0	55.7	37.1	Hydromagnesite 96.3; AF 3.7
400	Cake – K	+54.40	8.85	1.48	54.2	23.3	15.1	PE 35.9; BR 3.5; HM 37.0; KA 2.6; Magh 8.9; OM 12.1
	Filtrate – F		–	1.00	43.4	56.3	37.5	Hydromagnesite 97.5; AF 2.5
450	Cake – K	+48.38	9.28	1.66	59.0	16.7	10.5	PE 45.1; BR 4.8; HM 24.4; KA 3.0; Magh 9.3; OM 13.4
	Filtrate – F		–	0.67	43.3	55.7	37.0	Hydromagnesite 96.9; AF 3.1
500	Cake – K	+45.42	9.28	1.58	59.5	15.8	8.92	PE 44.1; BR 9.6; HM 20.4; KA 2.8; Magh 9.3; OM 13.8
	Filtrate – F		–	0.76	44.0	54.7	35.8	Hydromagnesite 93.5; AF 6.5
550	Cake – K	+37.58	8.92	1.40	63.4	13.1	7.68	PE 51.3; BR 6.6; HM 17.5; KA 2.5; Magh 8.9; OM 13.2
	Filtrate – F		–	1.07	43.2	55.1	36.1	Hydromagnesite 93.7; AF 6.3

Note: Chrs – chromspinels. In all cakes (K), the present chromspinels are included into the group of other minerals – OM.

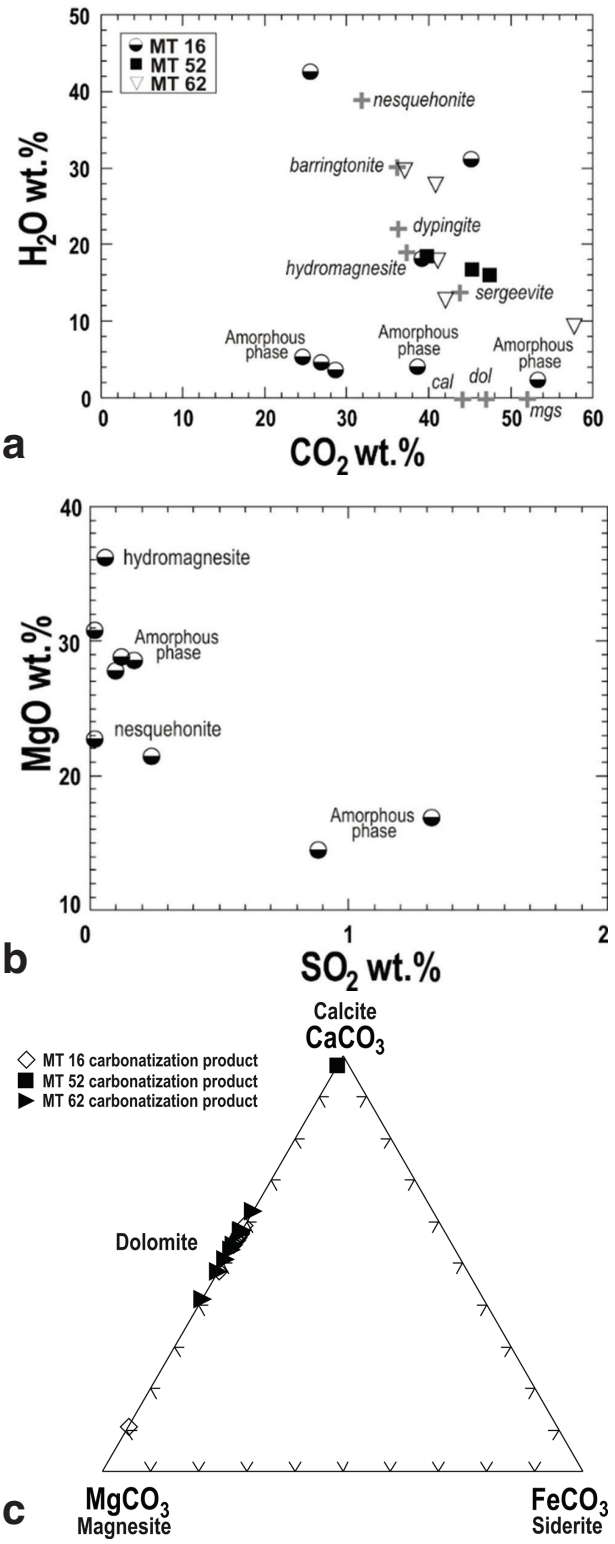

Fig. 3. Relation of fluid and amorphous phase in minerals after artifial carbonatization of chromium-magnesium waste. **a** – H_2O verzus CO_2; grey circles – acid carbonates and their standard chemical composition; **b** – content of MgO vs. SO_2 in minerals and amorphous phase of differing composition; **c** – chemical classification of calcite, dolomite and magnesite, originating after carbonatization of chromium-magnesium waste.

Tests with **changed durations of reactions** (Tab. 6) have revealed that the increments of the weight yields of compound products after carbonatization had reached after one hour increments +38,78 %, after two up to four hours ca 60 % and after more than five hours increments above +70 %. The highest increment was reached after 6 hours (+74.1 %). After all reactions the X-ray analysis revealed the origin of hydromagnesite in all products, but in filtration cakes there still remained periclase and brucite (their lowest content was after 6 hours – periclase 4.4 % and brucite 18.4 %, i.e. together 22.8 % in filtration cake).

Tests with **changed CO_2 pressures** (4–10 MPa; Tab. 6) at 2 hours lasting reactions. The increased CO_2 pressure (from 4 to 7 MPa) caused the total increase of the weight yield of compound product from +61.52 % to +69.28 %. At the pressure 8 and 10 MPa it was approximately balanced around +60 %. The primary laboratory temperature of suspension has increased at the CO_2 pressure 8.0 MPa and more and varied between 31–35 °C (Fig. 4a, b) due to the reaching the critical CO_2 pressure. Carbonatization products contain hydromagnesite, though the presence of input Mg minerals (periclase, brucite) was still revealed by the X-ray analysis. **The smallest content of these input minerals was at the CO_2 pressure 7 MPa after 2 hours of carbonatization** – periclase 12.9 % and brucite 11.0 %, i.e. together 23.9 % in filtration cake.

Increasing suspension density from 81 to 234 g/l (Tab. 6) has gradually increased the total compound carbonatized product (from +41.72 % to +68.16 %), though in all filtration cakes there are still present unreacted periclase and brucite. Precipitated products from filtrates contained 92.7–94.0 % of hydromagnesite. In filtration cakes with increasing density of suspension, the contents of periclase lowered from 49.9 % to 14.3 %, as well as brucite from 19.8 % to 7.3 %. At the same time the hydromagnesite content radically increased from 3.9 to 62.5 %.

Carbonatization parameters of the sample MT – verification of optimum conditions

Regarding all results of MT sample, **the best weight yield of compound product after carbonatization of the grist <0.1 mm was obtained at stirrer rotations 400 rpm, 6 hours reaction, input CO_2 pressure 6 MPa and suspension density 159 g/l (+74.1 %).** This reaction caused the depletion of the periclase and brucite content in filtration cake together to 22.8 %, which in comparison with input (75.6 %) represents depletion more than 3.3 times.

The second best result was reached at stirrer rotations **400 rpm after 2 hours, input pressure 7 MPa and suspension density 159 g/l (+69.28 %),** the decrease of periclase and brucite content in filtration cake represents 23.9 %. The hydromagnesite content in dried product from filtrate is 92.7 %. This second optimizing test was done at slightly higher pressure – increased from 6 MPa to 7 MPa, but the reaction time was distinctly shorter – 2 hours instead of 6 hours, which would have a positive impact on industrial practice.

Tab. 6
Results of the **MT** sample carbonatization tests – chemical and mineral composition in cakes and filtrates (wt.%) – applying fraction **<0.1 mm,** reaction temperature **22 °C** at sequentially changed reaction pressure, suspension density, stirrer rotation and duration of reaction with CO_2

Changed reaction parameter	Product	Total yield (wt.%)	Chemical composition (wt.%)					Mineral composition (wt.%)
			Fe_2O_3	CaO	MgO	Loss by ign.	CO_2	PE – periclase; BR – brucite; HM – hydromagnesite; KA – calcite; Magh – maghemite; AF – amorphous phase;
Changed duration of reaction (1–6 hours) at pressure **6 MPa,** suspension density **159 g/l** and stirrer rotation **400 rpm**								
MT	Input	–	7.57	2.09	78.3	0.37	0.33	PE 74.4; BR 1.2; KA 0.8; Chrs 12.6; Magh 7.5; AF 3.5
1	Cake – K	+38.78	9.57	1.59	60.2	16.0	7.65	PE 41.5; BR 16.5; HM 17.0; KA 2.8; Magh 9.6; OM 12.6
	Filtrate – F		–	–	43.8	54.4	35.7	Hydromagnesite 94.8; AF 5.2
2	Cake – K	+60.98	9.02	1.53	52.8	25.2	15.0	PE 30.0; BR 10.2; HM 36.7; KA 2.7; Magh 9.0; OM 11.4
	Filtrate – F		–	–	43.8	54.9	35.8	Hydromagnesite 95.1; AF 4.9
3	Cake – K	+59.38	8.96	1.30	53.6	24.2	14.9	PE 32.8; BR 7.1; HM 36.9; KA 2.3; Magh 9.0; OM 11.9
	Filtrate – F		–	–	43.3	55.0	35.3	Hydromagnesite 93.8; AF 6.2
4	Cake – K	+59.98	9.89	1.73	51.1	24.5	14.7	PE 29.2; BR 9.6; HM 35.4; KA 3.1; Magh 9.9; OM 12.8
	Filtrate – F		–	–	44.3	54.5	34.5	Hydromagnesite 91.6; AF 8.4
5	Cake – K	+71.12	5.94	1.03	45.6	39.0	23.2	PE 10.2; BR 14.1; HM 59.5; KA 1.8; Magh 5.9; OM 8.5
	Filtrate – F		–	–	42.9	53.9	33.8	Hydromagnesite 89.8; AF 10.2
6	Cake – K	+74.10	5.64	1.00	43.8	41.7	24.1	PE 4.4; BR 18.4; HM 61.9; KA 1.8; Magh 5.6; OM 7.9
	Filtrate – F		–	–	42.6	54.1	33.4	Hydromagnesite 88.7; AF 11.3
Changed CO_2 pressures (4–10 MPa) at **2 hour** reaction, stirrer rotation **400 rpm** and suspension density **159 g/l**								
4	Cake – K	+61.52	5.81	1.10	47.8	37.3	22.8	PE 15.4; BR 10.6; HM 58.3; KA 2.0; Magh 5.8; OM 7.9
	Filtrate – F		–	–	42.0	53.5	34.8	Hydromagnesite 92.4; AF 7.6
5	Cake – K	+62.04	5.97	0.98	47.6	37.1	22.6	PE 15.2; BR 10.8; HM 58.0; KA 1.8; Magh 6.0; OM 8.2
	Filtrate – F		–	–	42.0	54.0	35.3	Hydromagnesite 93.8; AF 6.2
6	Cake – K	+63.20	7.04	1.22	48.1	34.0	20.1	PE 17.0; BR 13.3; HM 50.8; KA 2.2; Magh 7.0; OM 9.7
	Filtrate – F		–	–	43.0	54.9	35.2	Hydromagnesite 93.5; AF 6.5
7	Cake – K	+69.28	6.30	1.06	46.0	37.9	23.1	PE 12.9; BR 11.0; HM 59.2; KA 1.9; Magh 6.3; OM 8.7
	Filtrate – F		–	–	42.8	54.6	34.9	Hydromagnesite 92.7; AF 7.3
8	Cake – K	+59.26	9.34	1.85	50.8	24.3	14.3	PE 28.4; BR 11.1; HM 34.1; KA 3.3; Magh 9.3; OM 13.8
	Filtrate – F		–	–	43.3	55.3	35.3	Hydromagnesite 93.8; AF 6.2
10	Cake – K	+60.92	8.58	1.53	49.9	27.8	15.9	PE 23.3; BR 14.2; HM 39.0; KA 2.7; Magh 8.6; OM 12.2
	Filtrate – F		–	–	43.3	55.0	34.5	Hydromagnesite 91.6; AF 8.4
Changed suspension density (81, 159, 234 g/l) at **2 hour** reaction, CO_2 pressure **6 MPa** and stirrer rotation **400 rpm**								
81	Cake – K	+41.72	10.50	0.85	65.3	9.0	2.13	PE 49.9; BR 19.8; HM 3.9; KA 1.5; Magh 10.5; OM 14.4
	Filtrate – F		–	–	42.7	54.2	35.4	Hydromagnesite 94.0; AF 6.0
159	Cake – K	+63.20	7.04	1.22	48.1	34.0	20.1	PE 17.0; BR 13.3; HM 50.8; KA 2.2; Magh 7.0; OM 9.7
	Filtrate – F		–	–	43.0	54.9	35.2	Hydromagnesite 93.5; AF 6.5
234	Cake – K	+68.16	5.76	0.97	46.3	38.6	24.3	PE 14.3; BR 7.3; HM 62.5; KA 1.8; Magh 5.8; OM 8.3
	Filtrate – F		–	–	41.4	53.2	34.9	Hydromagnesite 92.7; AF 7.3
Carbonatization tests at optimum conditions								
Temperature **22 °C,** CO_2 pressure **6 MPa,** suspension density **159 g/l,** stirrer rotation **400 rpm,** duration of reaction **6 hours**								
6 hours	K +52.72	+74.10	5.64	1.00	43.8	41.7	24.1	PE 4.4; BR 18.4; HM 61.9; KA 1.8; Magh 5.6; OM 7.9
	F +21.38		<0.05	2.41	42.6	54.1	33.4	Hydromagnesite 88.7; AF 11.3
Temperature **22 °C,** CO_2 pressure **7 MPa,** suspension density **159 g/l,** stirrer rotation **400 rpm,** duration of reaction **2 hours**								
2 hours	K +39.66	+69.28	6.30	1.06	46.0	37.9	23.1	PE 12.9; BR 11.0; HM 59.2; KA 1.9; Magh 6.3; OM 8.7
	F +29.62		0.10	1.74	42.8	54.6	34.9	Hydromagnesite 92.7; AF 7.3

Note: Chrs – chromspinels. In all cakes (K), the chromspines are included into group of other minerals – OM.

For verification and reproducibility of the results of CO_2 carbonatization at found optimum conditions, applying grist of the fraction **<0.1 mm** of the input sample MT, there were realized carbonatization tests at laboratory temperature **22 °C,** stirrer rotations **400 rpm,** suspension density **159 g/l,** CO_2 pressures **6 MPa** and **7 MPa** and two durations of reactions with CO_2 – **6, resp. 2 hours** (Tab. 6). Analyses of reaction products revealed the input Mg minerals (periclase and brucite) in summary content ca 23 % (ca 3.3-x depletion in comparison with input values). Next lowering of their content would be reached by further refinement of the sample, but it would increase a total cost for milling.

After carbonatization the filtration cakes (Fig. 1c) contain around 60 % of hydromagnesite with bound ca 23.5 % CO_2 (increase in comparison with the input value is ca 71-times). Products obtained by drying of filtrates (Fig. 1d) contain ca 90 % of hydromagnesite with bound ca 34 % of CO_2 (ca 103-times increase in comparison with the input value).

Two-stage carbonatization tests of the sample MT

Aiming to answer the question whether the total weight yield would be increased by the second carbonatization of the filtration cake 1 (obtained during the first carbonatization; **the filtration cake 1 still contains the remnant periclase and brucite**), we did two sets by three tests of the second carbonatization applying the input CO_2 pressures 6 MPa, resp. 7 MPa. Further reaction parameters: grist <0.1 mm, stirrer rotations 400 rpm and suspension density 159 g/l. Duration of carbonatization tests in the first and second carbonatization sets in hours: 1+1; 2+1 and 2+2 at both (6 and 7 MPa) input CO_2 pressures. The tests results are presented in Tab. 7, as well as Figs. 1e (filtration cake) and 1f (filtrate).

Tab. 7

Results of **two-stage MT sample carbonatization tests** aiming to lower the amount of brucite and periclase in carbonatization products. Input fraction **<0.1 mm,** reaction temperature **22 °C,** suspension density **159 g/l,** stirrer rotation **400 rpm.** CO_2 pressures differ in both test sequences (**6** and **7 MPa**)

Duration of reaction with CO_2	Products divided by filtration	Total yield (wt.%)	Chemical composition (wt.%)					Mineral composition (wt.%)
			Fe_2O_3	CaO	MgO	Loss by ign.	CO_2	PE – periclase; BR – brucite; HM – hydro-magnesite; KA – calcite; Magh – maghemite; AF – amorphous phase
MT	Input	–	7.57	2.09	78.3	0.37	0.33	**PE 74.4; BR 1.2;** KA 0.8; Chrs 12.6; Magh 7.5; AF 3.5
Carbonatization tests at 6 MPa								
1 hour	Filtrate 1	+47.88	<0.05	1.46	43.1	54.5	34.9	HM 92.7; AF 7.3
+1 hour reaction with cake 1	Cake 2	– 26.76	11.1	0.91	64.2	8.24	1.40	**PE 48.9; BR 21.0;** HM 1.8; KA 1.6; Magh 11.1; OM 15.6
	Filtrate 2	+19.62	<0.05	3.04	42.4	53.6	34.4	HM 91.4; AF 8.6
2 hours	Filtrate 1	+63.12	0.11	0.68	43.4	55.1	35.5	HM 94.3; AF 5.7
+1 hour reaction with cake 1	Cake 2	–32.46	12.1	1.20	60.5	8.97	2.57	**PE 46.2; BR 18.0;** HM 4.3; KA 2.1; Magh 12.1; OM 17.3
	Filtrate 2	+19.86	<0.05	3.70	41.5	54.8	35.4	HM 94.0; AF 6.0
2 hours	Filtrate 1	+61.80	0.10	0.91	43.0	55.5	35.6	HM 94.6; AF 5.4
+2 hours reaction with cake 1	Cake 2	–36.10	12.7	1.14	59.8	8.67	2.67	**PE 46.4; BR 16.5;** HM 4.7; KA 2.0; Magh 12.7; OM 17.7
	Filtrate 2	+25.52	0.08	2.73	42.6	53.8	34.6	HM 91.9; AF 8.1
Carbonatization tests at 7 MPa								
1 hour	Filtrate 1	+47.88	0.05	1.49	42.9	54.8	35.2	HM 93.5; AF 6.5
+1 hour reaction with cake 1	Cake 2	–26.76	12.1	0.94	62.9	7.61	1.50	**PE 49.2; BR 18.5;** HM 2.0; KA 1.7; Magh 12.1; OM 16.5
	Filtrate 2	+19.62	0.07	2.27	42.5	54.2	34.9	HM 92.7; AF 7.3
2 hours	Filtrate 1	+63.12	0.14	0.87	43.4	55.1	35.8	HM 95.1; AF 4.9
+1 hour reaction with cake 1	Cake 2	–32.46	12.9	1.19	59.0	8.23	2.05	**PE 43.5; BR 18.2;** HM 3.0; KA 2.1; Magh 12.9; OM 20.3
	Filtrate 2	+19.86	0.04	3.31	41.9	53.9	35.3	HM 93.8; AF 6.2
2 hours	Filtrate 1	+61.80	0.11	1.07	43.0	55.3	34.6	HM 91.9; AF 8.1
+2 hours reaction with cake 1	Cake 2	–36.10	13.6	1.17	57.5	7.90	2.28	**PE 44.9; BR 15.9;** HM 3.6; KA 2.1; Magh 13.6; OM 19.9
	Filtrate 2	+25.52	0.08	2.19	42.7	54.2	34.3	HM 91.1; AF 8.9

Note: Chrs – chromspinels. In all cakes the chromspines are included into group of other minerals – OM.

Table 7 demonstrates that lengthening of the total time of two-stage carbonatization from two (1+1), three (2+1) to four hours (2+2) has increased the weight yield of dried compound products from both filtrates in the order 67.5 % → 82.98 % → 87.32 % (pressure 6 MPa), resp. 78.96 % → 88.86 % → 93.10 % (pressure 7 MPa) with high content of hydromagnesite in them – from 91.1 % to 95.1 %, and simultaneously at the CO_2 pressure 7 MPa the yields of products are higher by ca 5.5 to 11.5 % at corresponding times.

The double-stage carbonatization from the viewpoint of fixation of CO_2 into the lattice of hydromagnesite applying the sample with the grist <0.1 mm is not perspective mainly due to the complexity and time demand of the whole process.

From 1 kg grist of the MT sample with grain-size beneath 0.1 mm there theoretically originate maximum 2.034 kg of the product (+103.4 %). At found optimum conditions of CO_2 mineral sequestration (6 MPa and 6 hours, resp. 7 MPa and 2 hours) and further optimum parameters (see above), there originates from the same amount of input sample altogether 1.741 kg of carbonatized product (+74.10 %), resp. 1.6928 kg of this product (+69.28 %), which represents in the first case the real reaching of 85.6 % conversion and in the second case 83.2 % conversion.

The course of some carbonatization parameters (CO_2 pressure, reaction temperature and stirrer rotations) during 2 hour carbonatization of the MT sample grist of 0.1 mm grain-size at optimum reaction conditions (pressure CO_2 7 MPa, temperature 22 °C, stirrer rotations 400 rpm, suspension density 159 g/l) is visualized in Fig. 4a, b.

Figure 4a shows that after the carbonatization has started (CO_2 purity 99.9 % obj.), the suspension temperature during first five minutes increased by ca 6 °C (from ca 25 °C to ca 31 °C), which manifests the exothermic reaction. The value of input CO_2 pressure from 7 MPa has gradually and linearly decreased during two hours of reaction. The similar reaction course was registered also in reaction with CO_2 purity 95 vol.% (Fig. 4b). The increase of the weight yields of both carbonatized products is comparable, i.e. +68.18 % (99.9 % purity of CO_2), resp. +67.96 % (95 % CO_2 +5 % air), which means that effective carbonatization can be done also applying CO_2 of the purity 95 vol.%.

The series of tests has demonstrated that the reaction of MgO mainly from input periclase and brucite with CO_2 has resulted at revealed optimum conditions with conversion 85.6 % (in the first case), resp. 83.2 % (in the second case), and in both cases there originated new mineral – hydromagnesite, in which lattice the CO_2 is safely, stable and permanently deposited.

The permanent binding of 1 tonne of CO_2 theoretically requires 1.4617 tonne of the chromium-magnesium waste (sample MT) with the grain-size <0.1 mm (ideal state). The reached carbonatization results at this material at optimum conditions manifest there is really possible to apply in the first case 1.708 t, resp. in the second case 1.757 t at sequestration of 1 tonne of CO_2, being bound in hydromagnesite.

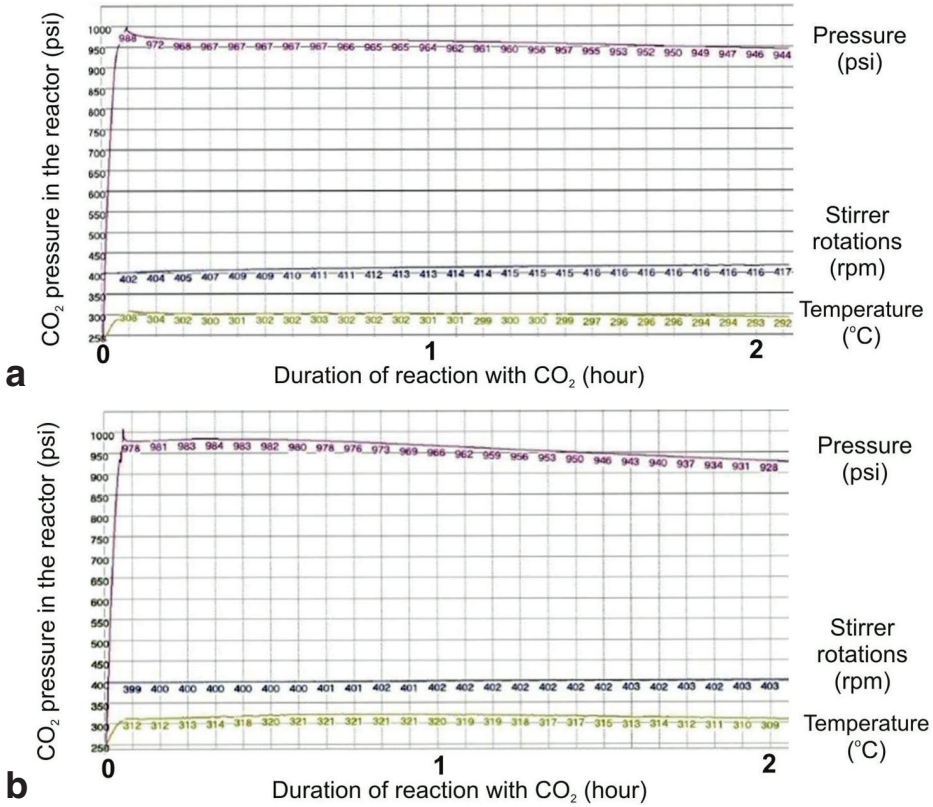

Fig. 4a, b. Graphs of final artificial carbonatization of the sample MT applying CO_2 with the purity 99.9 vol.% (a) and CO_2 with the purity 95.0 vol.% (b).

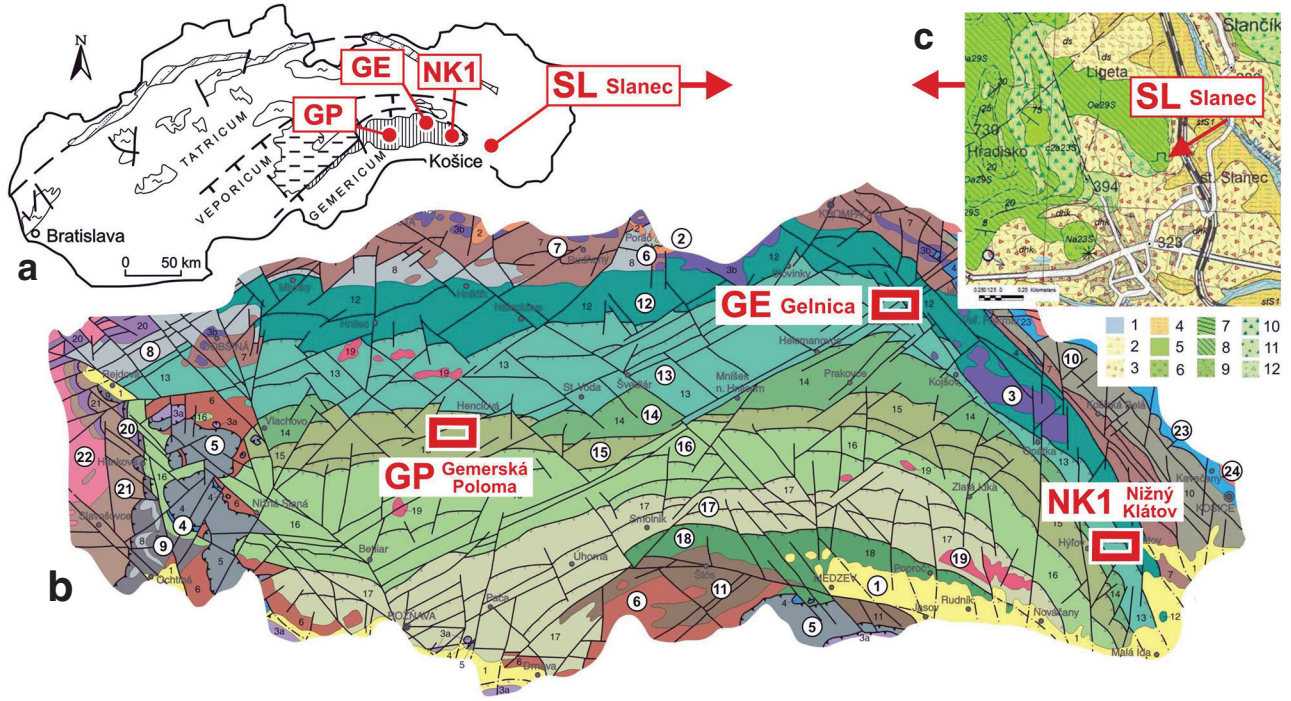

Fig. 5. a – Location of tested rock samples in Slovakia. **b** – Location of three rock samples from the Lower Paleozoic sequences of Gemericum – **GP** (Gemerská Poloma), **GE** (Gelnica) and **NK1** (Nižný Klátov) – is visualized in tectonic map of the Spiš-Gemer Ore Mts. (Grecula et al., 2009). 1 – Quaternary-Neogene sediments; 2 – Paleogene sediments of Subtatric Group; 3 – Silicicum; 4 – Meliaticum s.s.; 5 – Bôrka nappe (exhumed higher pressure sequences of Meliaticum). ***Upper Paleozoic:*** 6 – Gočaltovo Group; 7 – Krompachy Group; 8 – Dobšiná Group; 9 – Ochtiná Group; 10 – Črmeľ Group; 11 – Štós Group (Upper Devonian?-Lower Carboniferous). ***Lower Paleozoic:*** 12 – Rakovec Group; 13–19 – Gelnica Group: 13 – Kojšov zone; 14 – Mníšek zone; 15 – Prakovce zone; 16 – Humel zone; 17 – Jedľovec zone; 18 – Medzev zone; 19 – Permian granite. ***Veporicum:*** 20 – Föderata Group (Triassic cover); 21 – Revúca Group (Permian cover); 22 – crystalline basement. **c** – The sample **SL** (Slanec) represents Neogene volcanic rock of the Slanské vrchy Mts., as visualized in the map segment (Kaličiak et al., 1996): 1 – Holocene fluvial sediments; 2 – Pleistocene solifluction sediments; 3 – undivided Quaternary deluvial sediments. ***Lower Sarmatian-Lower Pannonian:*** *Stretava Fm.:* 4 – clays, claystones, siltstones with layers of tuffitic clay, sands. *Hradisko Fm.:* 5 – neck of hyperstene-augitic andesite; 6 – extrusion of pyroxenic andesite. *Bogota Fm.:* 7 – fine porphyric pyroxenic andesite. *Hradisko Fm.:* 8 – lava flows of hyperstene-augitic andesites; 9 – extrusion of augite-hyperstenic andesite; 10 – autochthonous pyroclastics: volcanic breccias, agglomerates, tuffs. *Bogota Fm.:* 11 – redeposited pyroclastics of pyroxenic andesites. *Hradisko Fm.:* 12 – epiclastic breccias to sandstones of pyroxenic andesites.

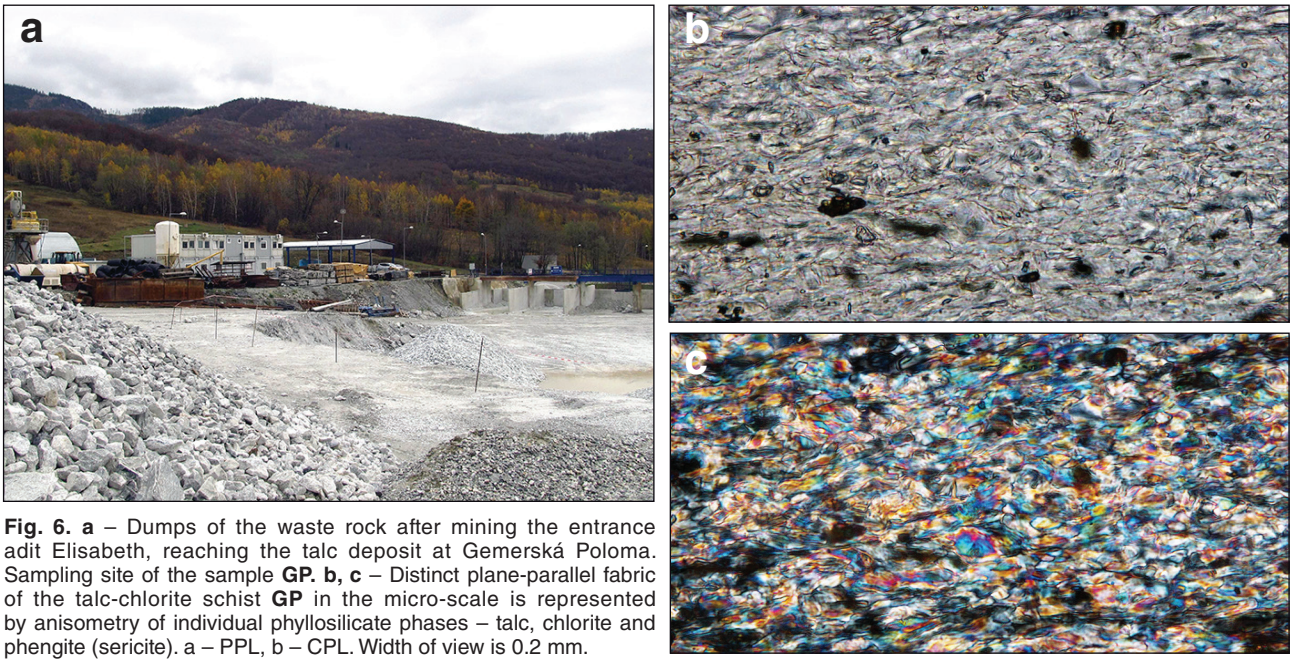

Fig. 6. a – Dumps of the waste rock after mining the entrance adit Elisabeth, reaching the talc deposit at Gemerská Poloma. Sampling site of the sample **GP. b, c** – Distinct plane-parallel fabric of the talc-chlorite schist **GP** in the micro-scale is represented by anisometry of individual phyllosilicate phases – talc, chlorite and phengite (sericite). a – PPL, b – CPL. Width of view is 0.2 mm.

Carbonatization of natural materials – the rock samples

The bearers of the Mg component in investigated four representative rock types from Slovak localities (Fig. 5) are the minerals talc (GP) and chlorite (GP, NK1, GE), the Ca component is present in amphibole (NK1) and plagioclase (NK1, GE, SL; Tab. 1). MgO varies in the range from 1.59 % (GE) to 22.4 % (GP), CaO from 0.16 % (GE) to 7.71 % (SL), though part of Ca component in some samples is bound on $CaCO_3$. Fe^{2+} as FeO ranges from 1.90 to 5.82 % (for comparison – in the chromium-magnesium waste it was 0.43 wt.%, Fe^{2+} is present in the structure of amphibole and chlorite (Tab. 1).

Talc-chlorite schist from locality Gemerská Poloma (GP)

The investigation of CO_2 sequestration potential of the sample of grey talc-chlorite schist (GP; Figs. 6a, 7a) from the mine dump at locality Gemerská Poloma was motivated by actual opening of the talc deposit and possible future availability of talc-chlorite schist as a waste material during exploitation of the talc deposit.

Sample GP was taken from the dump derived from the Elizabeth adit, which has reached the SW margin of the deposit. The Lower Paleozoic rock sequence with talc deposit, to which the sample **GP** relates, belongs to Gemericum – the Betliar Formation of the Gelnica Group and underwent complicated two-stadial evolution (Figs. 5a, b, 6; cf. Grecula et al., 2009).

Sample consisted dominantly of talc (29.4 %; Tab. 1) and chlorite (47.7 %), being a significant source of MgO component (22.40 wt.%), increasing the sequestration potential of the sample and partially also Fe^{2+} component, also appropriate for reaction with CO_2. Quartz (16.7 %) and sericite (6.2 %) do not dispose with sequestration potential.

The GP sample after grinding and milling to grain-size <0.5 mm has the chemical composition presented in Table 1, found by recalculation from XRD and chemical analyses. The homogeneous part of the grist <0.5 mm was further subjected to wet granulometric analysis (Tab. 8), whereby the weight yields of individual grain-size classes, total residua on nets, resp. throughs are related to dried state of the sample.

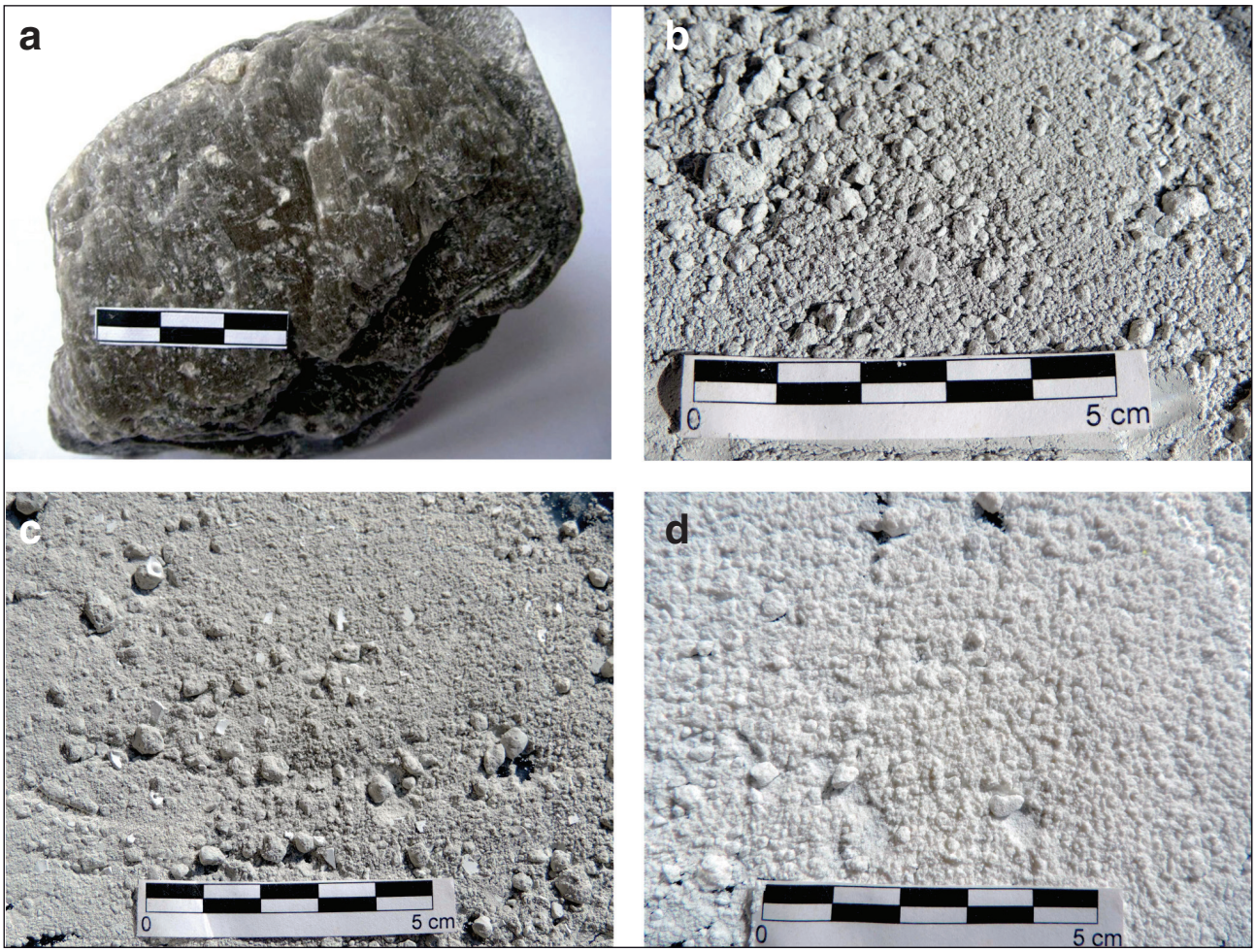

Fig. 7. a – Sample of the talc-chlorite schist; **b** – input talc-chlorite schist sample GPA after amorphization by milling; **c–d** – **GPA** carbonatization products: c – filtration cake, d – filtrate.

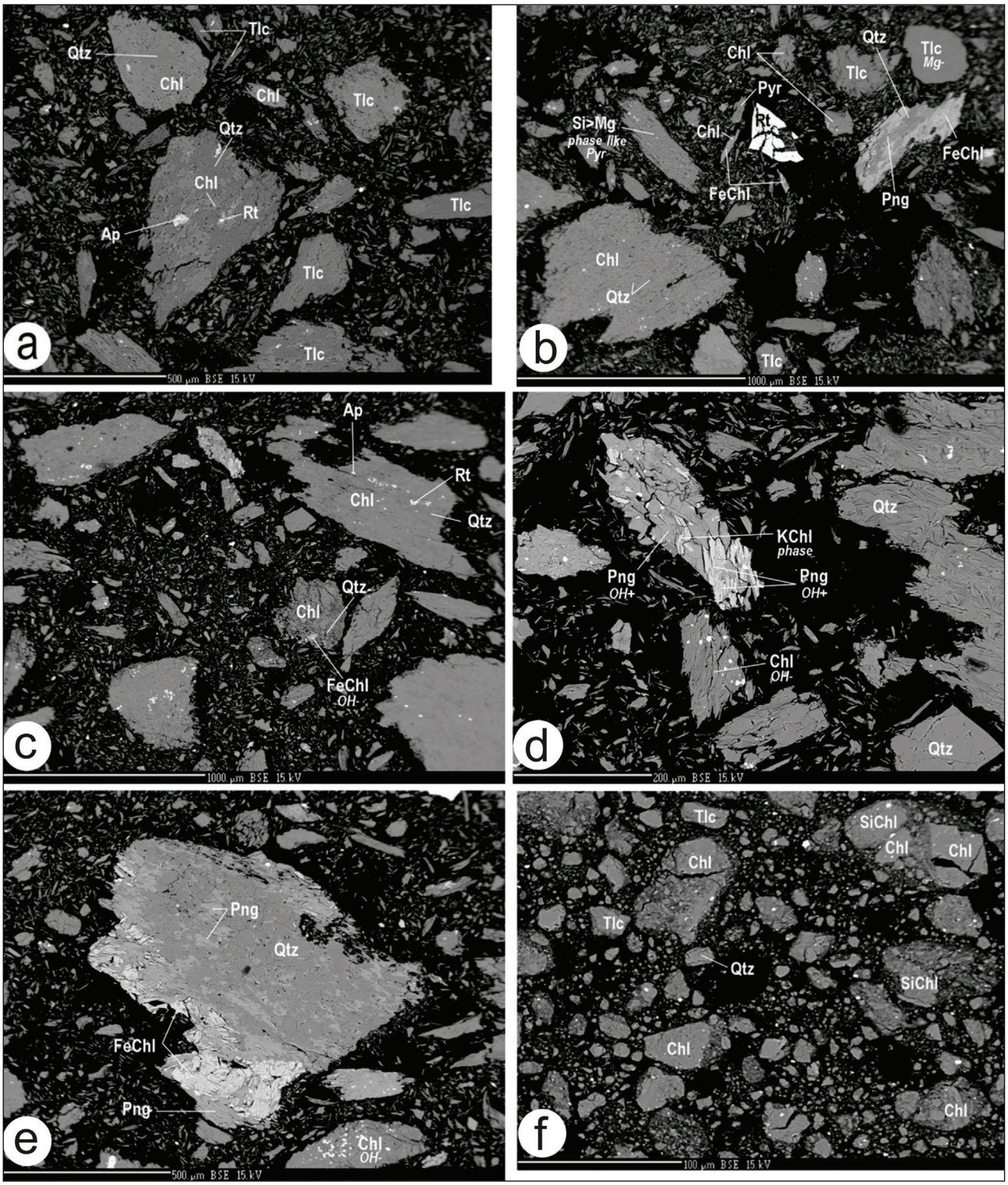

Fig. 8. a – Mineral composition of the input sample GP of the talc-chlorite schist from the dump at Gemerská Poloma. **b** – Composition of the thermally modified (700 °C) sample of talc-chlorite schists – **GP700. c–e** – Composition of thermally modified (925 °C) sample of talc-chlorite schists – **GP925. f** – Mechanically modified talc-chlorite schist – sample **GPA.** After amorphization by milling it is composed of a mixture of fragments without structural lattice. Tlc – talc; Chl – chlorite; FeChl – Fe chlorite; KChl – K chlorite; SiChl – Si chlorite; Rt – rutile; Ap – apatite; Qtz – quartz; Png – phengite; Pyr – pyrophyllite. BSE image.

Table 8 presents that in the grist of the input sample <0.5 mm the content of the finest grain-size class (<0.02 mm) is 58.74 %, which represents nearly 2/3 of the total amount of the sample. The CO_2 sequestration potential of the sample is indicated by 24.3 % of Mg and Fe^{2+} oxides.

The GP sample carbonatization tests were held in the reactor at five durations of reactions (1, 2, 3, 4 and 5 hours; Tab. 9) at input CO_2 pressure 6 MPa, suspension density 157 g/l and stirrer rotations 400 rpm – optimum rotations found at MT sample experiments. Further laboratory treatment corresponded with that at sample MT. If all MgO (22.4 %) and CaO (0.39 %) would fully react to Mg and Ca carbonates (without reaction of FeO), the maximum theoretical weight yield of the product after its reaction with CO_2 would represent an increase +29.9 %, i.e. from 1 kg sample with grain-size <0.5 mm there would originate 1.299 kg of carbonatized product. The laboratory tests aimed to gain this maximum weight yield of undivided product (+29.9 %), and the input mineral components – talc and chlorite should not be present there.

The artificial carbonatization of the talc-chlorite schists with a mixture of $H_2O + CO_2$ proceeds with some limitations according to reaction (2).

Tests at **different durations of reactions** (Tab. 9; **GP** sample) revealed that the increments of the total weight yields of compound products after carbonatization of the sample grist in the reactor were low and ranged from +0.38 % to +0.82 % in duration from 1 to 5 hours. Products from dried filtrates contained precipitated $CaCO_3$. The highest increment was found after 5 hour reaction (+0.82 %). At all durations of reactions with CO_2, XRD has demonstrated in products from filtrates the crystallization of aragonite + calcite and after 5 hours also of hydromagnesite. The filtration cakes have identified also preserved original minerals with unreacted Mg components with CO_2 at given carbonatization conditions neither after 5 hours due to insufficient deliberation of given components from the lattice of given minerals – talc and chlorite.

Based on previous results, the grist of the **GP** sample underwent thermic activation at temperatures 700 °C **(GP700),** resp. 925 °C **(GP925)** aiming at least partially destruct the chlorite, eventually talc lattice.

The reactivity of CO_2 mainly with MgO component of the sample **GP700,** resp. **GP925** were performed in the high-pressure reactor at **eight durations of reactions with CO_2** (1, 2, 3, 4, 5, 6, 12 a 24 hours; Tab. 9) at input CO_2 pressure 6 MPa, suspension density 157 g/l, stirrer rotations 400 rpm.

In the case of sample **GP700** the total weight yields of compound products after carbonatization were low and slightly increased from +0.38 % to +0.64 % in time sequence from 1 to 24 hours. The products of gained filtrates contained precipitated $CaCO_3$. The supreme

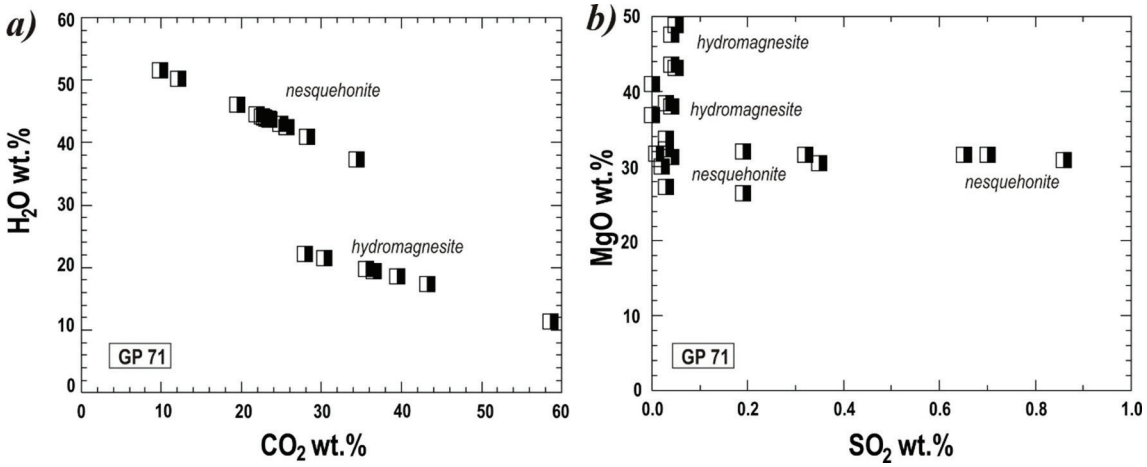

Fig. 9. Chemical classification of minerals and relation of the fluid phase H_2O vs. CO_2 and MgO vs. SO_2 in minerals – products of artificial carbonatization of the talc-chlorite schist. Minerals crystallized at 200 °C. Sample GP (filtrate).

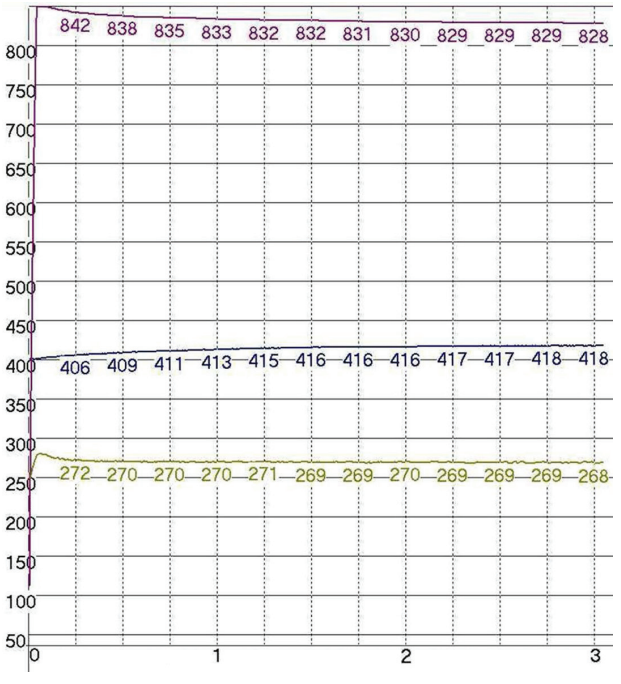

Fig. 10. Curves of pressure (psi, upper curve), stirrer rotation (rpm, middle curve) and temperature (°C, lower curve) during 3 hour carbonatization of the sample **GPA,** applying CO_2 with the purity 99.9 %.

increase was reached after 24 hours (+0.64 %). During all durations of reactions the origin of aragonite (+calcite) was revealed, after 5 hours it was also hydromagnesite. In filtration cakes there were still identified also original input minerals, which Mg component has not reacted with CO_2 at given carbonatization conditions neither after 24 hours, due to its insufficient deliberation from the lattice of appropriate minerals.

Tab. 8
Wet granulometric analysis of the grist of tested four rock samples

Grain-size class (mm)	Weight yield (%)		
	Class	Total residue	Total fall through the sieve
Wet granulometric analysis of the **GP sample grists of talc-chlorite schist**			
0.2–0.5	0.09	0.09	–
0.1–0.2	3.05	3.14	99.91
0.063–0.1	8.42	11.56	96.86
0.045–0.063	6.79	18.35	88.44
0.020–0.045	22.91	41.26	81.65
–0.020	58.74	–	**58.74**
Sum	100.00	–	–
Wet granulometric analysis of the **NK1 sample grists of metabasic rock**			
0.2–0.5	1.22	1.22	–
0.1–0.2	12.48	13.70	98.78
0.063–0.1	12.43	26.13	86.30
0.045–0.063	7.45	33.58	73.87
0.020–0.045	19.90	53.48	66.42
–0.020	46.52	–	**46.52**
Sum	100.00	–	–
Wet granulometric analysis of the **GE sample grists of chlorite schist**			
0.2–0.5	0.83	0.83	–
0.1–0.2	8.59	9.42	99.17
0.063–0.1	11.07	20.49	90.58
0.045–0.063	7.20	27.69	79.51
0.020–0.045	17.74	45.43	72.31
–0.020	54.57	–	**54.57**
Sum	100.00	–	–
Wet granulometric analysis of the **SL sample grists of pyroxene andesite**			
0.2–0.5	2.45	2.45	–
0.1–0.2	20.92	23.37	97.55
0.063–0.1	14.35	37.72	76.63
0.045–0.063	8.81	46.53	62.28
0.020–0.045	18.56	65.09	53.47
–0.020	34.91	–	**34.91**
Sum	100.00	–	–

Tab. 9
Carbonatization tests of the talc-chlorite schist grist **without thermic activation (GP),** as well as the grist **with thermic activation at 700 °C (GP700)** and **925 °C (GP925).** Reaction parameters: temperature **22 °C,** CO_2 pressure **6 MPa,** suspension density **157 g/l,** stirrer rotation **400 rpm** and differing duration of reaction with **CO_2 – 1–5 hours (GP) and 1–6, 12 and 24 hours (GP700, GP925)**

Duration of reaction (hour)	Product	Total yield (wt.%)	Mineral composition (wt.%)
			TL – talc; CHL – chlorite; KR – quartz; SE – sericite; AF – amorphous phase
GP	Input	–	TL 29,4; CHL 47,7; KR 16,7; SE 6,2
	Cake	–	Chlorite, talc, quartz, sericite
1	Filtrate	+0.38	Aragonite (+calcite), AF
2	Filtrate	+0.42	Aragonite (+calcite), AF
3	Filtrate	+0.64	Aragonite (+calcite), AF
4	Filtrate	+0.48	Aragonite (+calcite), AF
5	Filtrate	+0.82	Aragonite (+calcite), hydromagnesite, AF
GP700	Input	–	Chlorite, talc, quartz, sericite
	Cake	–	Chlorite, talc, quartz, sericite
1	Filtrate	+0.38	Brucite, aragonite (+calcite), AF
2	Filtrate	+0.38	Brucite, aragonite (+calcite), AF
3	Filtrate	+0.42	Brucite, aragonite, AF
4	Filtrate	+0.42	Brucite, aragonite, AF
5	Filtrate	+0.44	Brucite, aragonite, hydromagnesite; AF
6	Filtrate	+0.42	Brucite, aragonite, hydromagnesite; AF
12	Filtrate	+0.54	Brucite, aragonite (+calcite?), hydromagnesite; AF
24	Filtrate	+0.64	Brucite, aragonite (+calcite?), hydromagnesite; AF
GP925	Input	–	Quartz, talc, sericite, clinoenstatite, olivine?
	Cake	–	Quartz, talc, clinoenstatite, olivine?, AF
1	Filtrate	+0.34	Brucite, AF
2	Filtrate	+0.26	Brucite, aragonite (+calcite), AF
3	Filtrate	+0.32	Brucite, aragonite (+calcite), AF
4	Filtrate	+0.20	Brucite, aragonite (+calcite), AF
5	Filtrate	+0.24	Brucite, aragonite (+calcite), AF
6	Filtrate	+0.26	Brucite, aragonite (+calcite), AF
12	Filtrate	+0.38	Brucite, aragonite (+calcite), AF
24	Filtrate	+0.40	Brucite, aragonite (+calcite), AF

6 MPa, 22 °C, 3 hours

$$\underset{\text{talc}}{Mg_6Si_8O_{20}(OH)_4} + 7CO_2 + 7H_2O \rightarrow \underset{\text{hydromagnesite}}{Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O} + \underset{\text{nesquehonite}}{Mg(CO)_3{\cdot}3H_2O} + \underset{\text{opal}}{8SiO_2{\cdot}nH_2O} \quad (2)$$

Table 9 further manifest that the increments of total weight yield of compound products after carbonatization of the sample **GP925** were low and varied from +0.20 % to +0.40 % in reaction duration from 1 to 24 hours. $CaCO_3$ has precipitated in products obtained by drying of filtrates. The highest increase was reached after 24 hours (+0.40 %), though at all durations of reaction (besides that after 1 hour) the XRD analyses proved aragonite (+calcite) in products from filtrates after carbonatization. Hydromagnesite was not identified in any product obtained by drying of filtrate, present there was only brucite. In filtration cakes there were identified two primary input minerals (quartz and talc), as well as new clinoenstatite and olivine(?), which have originated at thermic activation of original sample GP at temperature 925 °C from Mg and Si component from chlorite and partly from talc. The Mg component from the sample GP925 has not reacted with CO_2 at given carbonatization conditions even after 24 hours of reaction.

The results presented in Table 9 manifest that neither mechanical (3 hour milling of the sample GP), nor thermic activation of the sample (annealing of the GP sample grist at 700, resp. 925 °C) has released the Mg component from the lattices of chlorite and talc, resp. released it only in a small extent, therefore the carbonatization reaction was inefficient.

From above stated reasons the input sample GP was milled to such level (amorphization of the sample – **GPA**) that at milling the lattices of talc, chlorite and sericite were destructed, which deliberated Mg component and this reacted with water in suspension transitionally to brucite and brucite at carbonatization reacted with CO_2 to hydromagnesite (Turianicová et al., 2013). After milling of the GP sample the specific surface has increased from former 1.1123 m^2/g to 10.8177 m^2/g – **GPA.**

Carbonatization tests of the sample GPA (amorphized sample GP)

Reactivity tests of CO_2 with MgO component of amorphized sample **GPA** were realized in the high pressure reactor at **five durations of reactions with CO_2** (1, 3, 6, 12 and 24 hours), **four CO_2 pressures** (4, 6, 8 and 10 MPa) and **three suspension densities** (156, 223 and 289 g/l) at stirrer rotations 400 rpm (Tab. 10). The test aimed to approach the theoretical increase of the weight yield of undivided (compound) product (+29.9 %).

Table 10 manifests that at **different duration of reaction with CO_2** the weight yields in compound products have increased after carbonatization of amorphized sample by +3.69 % (1 hour) to +7.54 % (24 hours). In all durations of the CO_2 reaction there was proved by XRD analysis the formation of hydromagnesite (its content of hydromagnesite, resp. CO_2 have increased in relation to prolongation of carbonatization from 80.0 % to 85.3 %, resp. from 30.1 % to 32.1 %). In filtration cakes there remained present only quartz and amorphous phase.

Concerning the different **CO_2 pressures** (4 to 10 MPa; Tab. 10) at 3 hour duration of suspension reaction with CO_2, the increase of total weight yield of compound product was negligible – from +5.09 % to +5.94 %. The suspension temperature at input pressure of CO_2 8.0 MPa and more during increasing pressures has increased from 31 to 35 °C owing to reaching the CO_2 critical state.

The carbonatization products (from filtrates) contained newly formed hydromagnesite in a range 82.1 % up to 90.0 %, in which the CO_2 was bound in the range 30.9 % to 33.9 %.

Testing various densities of suspension from 156 to 289 g/l there is visible (Tab. 10) that increasing density caused negligible decrease of total weight yield of carbonate product (from +5.34 % to +4.76 %). The precipitated products from filtrates contained 87.6–92.4 % of hydromagnesite binding CO_2 from 33.0 to 34.8 %.

Amorphization of the sample GP caused that the sample **GPA** had an increase of the weight yield of compound (undivided) carbonatized products from +3.69 % to +7.54 % (in average 5.62 %), i.e. ca 11-times higher than the value at the sample **GP** (from +0.2 % to 0.82 % – in average 0.51 %).

Next test at temperature **22 °C,** input CO_2 pressure **6 MPa,** suspension density **156 g/l,** stirrer rotation **400 rpm** and reaction duration **3 hours,** applying amorphous sample **GPA,** has produced the filtration cake (Fig. 7c) and filtrate (Fig. 7d). The dried product of filtrate has manifested an increase of the weight yield of compound carbonatized product +5.44 %, which represents 5.5-times lower value than is the value of theoretical increase (+29.9 %). Table 11 summarizes the results of this test. The graphic visualization of the pressure (psi), stirrer rotations (rpm) and temperature (°C) courves, presented in Fig. 10, indicates that immediately after the carbonatization has started (CO_2 purity of 99.9 vol.%) during ca 2–3 minutes, the suspension temperature in the reactor has increased from ca 22 °C to ca 28 °C, which manifests the exothermic reaction course. Decrease of the value of input CO_2 pressure during 3 hours is very slow and gradual and has after 15 minutes to 3 hours ideal linear trend.

As follows from the above stated, the reaction mainly of MgO from amorphized input minerals (chlorite, talc) with CO_2 after 3 hours was more effective than in the case of **GP** sample in corresponding time. In the dry product from the filtrate there is present 86.6 % of hydromagnesite with bound 32.6 % CO_2 (increase in comparison with the input is by 32.53 %).

During amorphization of appropriate input minerals (talc and chlorite) by the sufficiently long milling of GP sample, mainly the dominanting Mg component is activated for the reaction with CO_2. In the case of reacting the whole amount of Mg component and eventually Ca component with CO_2 to hydromagnesite and eventually $CaCO_3$ (100 % conversion), the sequestration potential is 5.031 tonnes of amorphized talc-chlorite schist (sample GPA) for binding of 1 tonne of CO_2.

Metabasic rock from the locality Nižný Klátov (NK1)

The tested sample was taken from the outcrop of exhumed melange of tectonized Paleozoic metabasic rocks of Rakovec Group in tectonic position on Gelnica Group (Gemericum; cf. Grecula et al., 2009) in the cut of the state

Tab. 10
Carbonatization results of **amorphous grind of talc-chlorite schist GPA** at sequentially changed duration of reaction with CO_2, the reaction pressures and suspension density. The temperature **22 °C** and stirrer rotation **400 rpm** are constant

Changed reaction parameter	Product	Total yield (wt.%)	Chemical composition (wt.%)							Mineral composition (wt.%)
			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Ign. loss	CO_2	KR – quartz, AF – amorphous phase
GPA	Input	–	51.7	12.7	2.88	0.39	22.4	7.74	0.07	Quartz, amorphous phase
Changed duration of reaction: 1, 3, 6, 12 and 24 hours										
1	Cake – K	+3.69	49.3	12.9	2.94	0.40	20.8	11.1	0.20	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.60	43.1	52.1	30.1	Hydromagnesite 80.0; AF 20.0
3	Cake – K	+5.06	50.2	13.2	3.02	0.29	20.4	10.3	0.14	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.43	42.9	53.6	30.9	Hydromagnesite 82.1; AF 17.9
6	Cake – K	+5.40	50.9	13.3	3.07	0.34	20.3	9.54	0.16	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.41	43.0	53.0	31.4	Hydromagnesite 83.4; AF 16.6
12	Cake – K	+6.56	50.2	12.9	3.05	0.28	20.1	10.7	0.29	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.43	43.1	54.5	31.6	Hydromagnesite 83.9; AF 16.1
24	Cake – K	+7.54	51.3	13.2	3.12	0.29	19.7	9.87	0.07	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.36	42.9	55.3	32.1	Hydromagnesite 85.3; AF 14.7
Changed CO_2 pressures (4, 6, 8 and 10 MPa) at 3 hours duration of reaction										
4	Cake – K	+5.09	–	–	–	0.58	23.6	9.29	0.06	Quartz, amorphous phase
	Filtrate – F		–	–	–	1.89	43.4	52.4	32.4	Hydromagnesite 86.1; AF 13.9
6	Cake – K	+5.34	–	–	–	0.36	20.8	9.33	0.02	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.81	44.2	52.8	33.0	Hydromagnesite 87.6; AF 12.4
8	Cake – K	+5.74	–	–	–	0.39	20.7	9.30	0.09	Quartz, amorphous phase
	Filtrate – F		–	–	–	1.22	43.9	52.2	30.9	Hydromagnesite 82.1; AF 17.9
10	Cake – K	+5.94	–	–	–	0.38	20.4	9.33	0.01	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.76	42.9	53.8	33.9	Hydromagnesite 90.0; AF 10.0
Changed suspension density (156, 223 and 289 g/l) at 3 hours reaction and CO_2 pressures 6 MPa										
156	Cake – K	+5.34	–	–	–	0.36	20.8	9.33	0.02	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.81	44.2	52.8	33.0	Hydromagnesite 87.6; AF 12.4
223	Cake – K	+4.97	–	–	–	0.36	20.6	9.34	0.10	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.43	43.7	54.6	34.8	Hydromagnesite 92.4; AF 7.6
289	Cake – K	+4.76	–	–	–	0.36	20.2	9.52	0.02	Quartz, amorphous phase
	Filtrate – F		–	–	–	0.40	44.1	54.5	34.7	Hydromagnesite 92.2; AF 7.8

Tab. 11
Chemical and mineral composition of divided carbonatization products of the sample **GPA**

Chemical composition of **filtration cake – K** (wt.%)							
GPA	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2
+5.44 %	55.4	14.5	3.21	1.01	0.36	14.2	0.90
MnO	K_2O	Na_2O	P_2O_5	Cr_2O_3	SO_3	Ign. loss	CO_2
0.01	0.84	<0.2	0.22	0.0042	0.38	9.77	<0.01
Chemical composition of the **product from filtrate – F** (wt.%)							
GPA	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2
+5.44 %	1.92	0.10	0.02	<0.01	0.46	43.9	<0.01
MnO	K_2O	Na_2O	P_2O_5	Cr_2O_3	SO_3	Ign. loss	CO_2
0.01	0.05	<0.2	0.02	0.0349	0.26	53.3	32.6
Mineral composition of **filtration cake – K** (wt.%)							
quartz				Si, Al, Fe,...amorphous phase			
Mineral composition of the **product from filtrate – F** (wt.%)							
hydromagnesite		86.6		Mg–Si amorphous phase		13.4	

road between villages Nižný Klátov and Hýľov ca 200 m to WNW of the deviated road to Nižný Klátov (Figs. 5a, b and 11a). Coordinates: 48°43`32.70``N, 21°08`29.99``E.

Sampled outcrop (Fig. 11a, b) consisted of a variety of tectonically converged lithological types (basalts, metagabbros, chloritic schists). They, similarly as in the case of other occurrences of basaltic to gabbroid rocks in the Rakovec Group in Gemericum, represent the exhumed tectonic mélange. Rocks in outcrop manifest double tectonometamorphic overprint: The prograde and retrograde metamorphism related to Variscan exhumation deformation phase VD_1 (sensu Németh in Radvanec et al., 2007) is represented with plastic foliation planes dipping generally to NNE. The younger Alpine overprints during the overthrust phase AD_1 and strike-slips during the phase AD_3 (l.c.) have produced the cleavage planes dipping to SSW, bearing the indications of subhorizontal transpression shears (Fig. 11b).

Input sample **NK1** (Fig. 13a) is characteristic with distinct plastic deformation (Fig. 12) with asymmetric microstructures (rotated porphyroclasts, etc.). Minerals having light interference colours are represented with dominantly present basic plagioclases, as well as calcite, dark grains are formed with amphiboles (actinolite) and chlorite. Less abundant are epidote and titanite.

The pre-reaction laboratory preparatory procedures were the same as at samples **MT** and **GP.** The chemical and mineral compositions of the sample **NK1** is stated in Table 1, the wet granulometric analysis of the grist is in the Table 8.

As manifested in Tab. 8, the grist of the input sample **NK1** with the grain-size <0.5 mm contains 46.52 % of the finest class (<0.02 mm), which represents nearly half of the whole sample amount. From chemical and mineral composition (Tab. 1) there follows that the sample contains amphibole with Ca, Mg and Fe^{2+} bound in its structure, next chlorite – Mg and Fe^{2+} components and plagioclase (Ca components), being appropriate for reaction with CO_2. Next present minerals – calcite and further Si-, Al- and Fe-oxides do not provide suitable components for carbonatization reactions.

The sequestration potential of the **NK1** sample grist is manifested with a total value of 19.72 % of Ca, Mg and Fe^{2+} oxides.

Carbonatization tests of the grist of NK1 sample

The CO_2 reactivity tests with the "free" CaO and all MgO, event. Fe^{2+} components of the sample **NK1** were done in the high-pressure reactor at **five CO_2 reaction times** (1, 3, 6, 12 and 24 hours), **five input CO_2 pressures** (2, 4, 6, 8 and 10 MPa) and **four suspension densities** (156, 230, 299 and 368 g/l; Tab. 12) at stirrer rotations 400 rpm (optimum rotations found at experiments with the waste material **MT**).

In the optimum case of reacting the whole MgO content (7.57 %) and "free" CaO (4.56 %) of the sample **NK1** for Mg and Ca carbonates (without reaction of FeO), the maximum theoretical increase of the weight yield of undivided product after reaction with CO_2 would represent an increase +13.6 %, i.e. from 1 kg of the sample with the grain-size <0.5 mm there would originate 1.136 kg of carbonatized product.

The artificial carbonatization of metabasic rock with the mixture of H_2O + CO_2 proceeds in limited extent according to following reactions (3) and (4).

As demonstrated in Table 12, at **different durations of reactions with CO_2** (1–24 hours) the increases of weight yields of carbonatization products were low and varied in the range from +1.28 % to +1.48 %. The products obtained by drying contain $CaCO_3$. The biggest increase was provided by 6 hours lasting reaction (+1.48 %). In filtrates, the XRD analyses of carbonatization products of all reactions durations have manifested the presence of newly formed aragonite + calcite. In filtration cakes there were identified also former input minerals, which Ca and Mg components did not react with CO_2 at given carbonatization conditions even after 24 hours of reaction due to their insufficient deliberation from the lattice of given minerals.

Testing at **different CO_2 pressures** (2–10 MPa) during 1 hour reaction (Tab. 12) revealed that at input

Fig. 11. a – Location of sampled mélange-type outcrop of exhumed metagabbro in the southern vicinity of the Nižný Klátov village. Orthophotomap is from the Google Earth. **b** – Double tectonic overprint in sampled outcrop: Younger Alpine brittle-ductile cleavage is a result of transpression deformation. The sample **NK1** was taken from the rigid block with pervasive Variscan ductile deformation and recrystallization, being less deformed by the younger Alpine shearing.

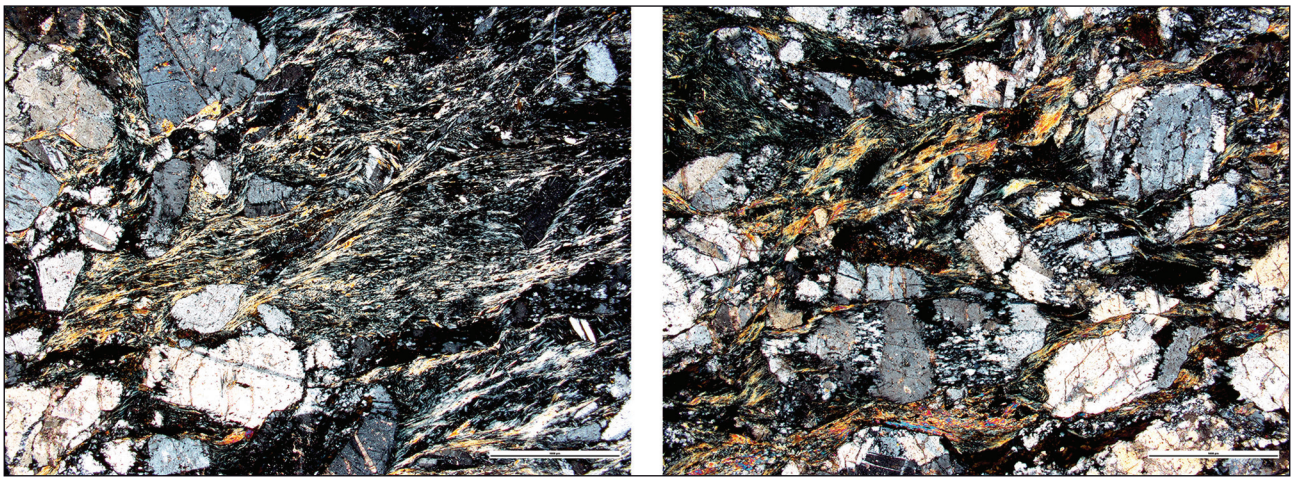

Fig. 12. Ductile deformation in mylonitized metabasic rock **NK1** during the VD_1 phase is manifested by rotated porphyroclasts of rheologically harder minerals (preferably plagioclase and diopside) in soft phyllosilicate matrix. Cross-polarized light, width of view 4.75 mm.

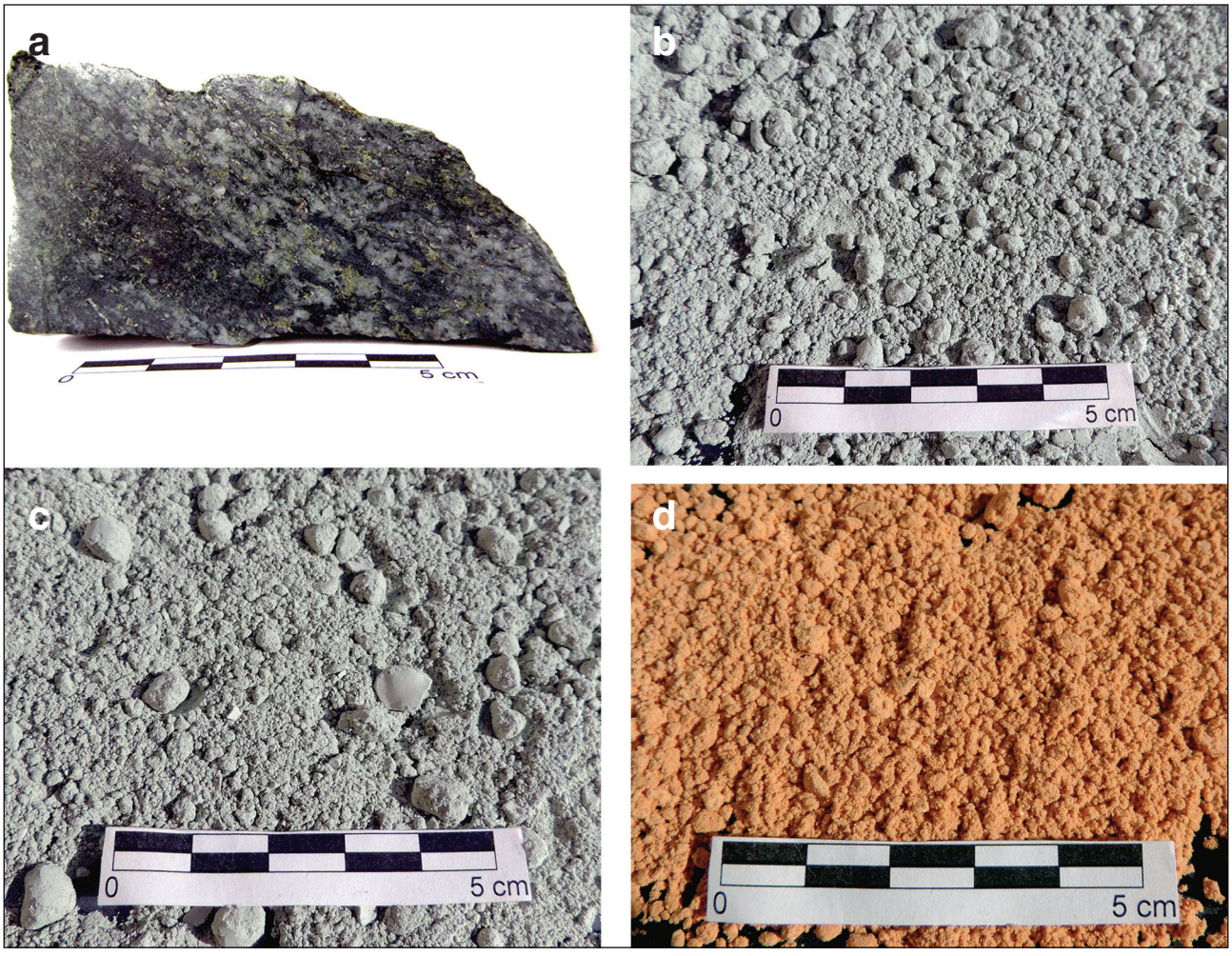

Fig. 13. Tested sample of the metabasic rock NK1. **a** – hand-sample; **b** – input grist <0.5 mm; **c–d** – carbonatization products: c – filtration cake, d – filtrate.

CO_2 pressure ≤4 MPa the total increase of the weight yield of carbonatization product was beneath +1.0 %. At pressures ≥6 MPa it was above 1.0 %. Achieving of the CO_2 supercritical state (temperature above 31.1 °C and pressure above 7.39 MPa) is relatively demanding from economical, time and technical viewpoints. Taking into account this fact and the results in Tab. 12, as the most appropriate there was determined the CO_2 pressure 6 MPa. Carbonatization products from filtrates contain newly formed aragonite + calcite, though the former input minerals still remained in filtration cakes.

Tests at **different suspension densities** (Tab. 12) revealed that the total increase of the weight yield in each case was corresponding to ca +1.1 %. The dried products from filtrates contained $CaCO_3$ in the form of aragonite and calcite. Therefore as appropriate there can be supposed the suspension densities in the range 156–368 g/l.

As Table 12 clearly manifests, the increase of the weight yield of majority of undivided carbonatized products was only around +1.1 to +1.4 %, i.e. ca 10-times lower that the value of theoretical increase (+13.6 %). For the complete chemical and mineralogical characteristic of the NK1 carbonatization course, we did a test at with **NK1** sample grist <0.5 mm at following conditions: temperature **22 °C,** input CO_2 pressure **6 MPa,** suspension density **156 g/l,** stirrer rotation **400 rpm** and duration of CO_2 reaction **3 hours.** Products after subsequent filtration of suspension and obtaining the filtration cake and filtrate are shown in Fig. 13c, d. The increase of the weight yield of carbonatized product was +1.3 %. The summarized results of this test with CO_2 of purity 99.9 % are provided by Table 13. From the courses of pressure, temperature and rotations during this carbonatization, shown in Fig. 16, there is visible that during first ca 1 minute the suspension temperature in the reactor has increased from ca 22 °C to ca 27 °C, which proves the exothermic reaction. The pressure drop during 3 hour lasting reaction was very slow, and in time interval from 10 minutes to 3 hours has a linear trend.

$$\underset{\text{plagioclase}}{CaAl_2Si_3O_8} + CO_2 + 5H_2O \rightarrow \underset{\text{calcite}}{CaCO_3} + \underset{\text{allophanite-amorphous phase}}{Al_2O_3{\cdot}(SiO_2)_{1.3-3}{\cdot}(H_2O)_{2.5-3}} \quad (3)$$

$$\textbf{Epidote-zoisite} + CO_2 + H_2O \rightarrow \textbf{calcite + Al-Si-OH amorphous phases} \quad (4)$$

Tab. 12
Carbonatization results of the grist of metabasic rock sample **NK1,** applying reactions at temperature **22 °C,** stirrer rotations **400 rpm** and differing duration of reactions, CO_2 pressure and density of suspension

Changed reaction parameter	Product	Total yield (wt.%)	Mineral composition (wt.%)
			PL – plagioclase; AM – amphibole; CHL – chlorite; CC – calcite; OC – other components
NK1	Input	–	PL 42.9; AM 31.5; CHL 21.1; CC 3.2; OC 1.3
Changed duration of reaction (1, 3, 6, 12, 24 hours) at pressure 6 MPa and suspension density 156 g/l			
	Cake	–	Plagioclase, amphibole, chlorite, calcite
1	Filtrate	+1.28	Aragonite, calcite, amorphous phase
3	Filtrate	+1.28	Aragonite, calcite, amorphous phase
6	Filtrate	+1.48	Aragonite, calcite, amorphous phase
12	Filtrate	+1.38	Aragonite, calcite, amorphous phase
24	Filtrate	+1.34	Aragonite, calcite, amorphous phase
Changed CO_2 pressures (2, 4, 6, 8, 10 MPa) at 1 hour lasting reactions and suspension density 156 g/l			
	Cake	–	Plagioclase, amphibole, chlorite, calcite
2	Filtrate	+0.74	Aragonite, calcite, amorphous phase
4	Filtrate	+0.90	Aragonite, calcite, amorphous phase
6	Filtrate	+1.14	Aragonite, calcite, amorphous phase
8	Filtrate	+1.24	Aragonite, calcite, amorphous phase
10	Filtrate	+1.40	Aragonite, calcite, amorphous phase
Changed suspension density (156, 230, 299 and 368 g/l) at 1 hour lasting reactions and CO_2 pressures 6 MPa			
	Cake	–	Plagioclase, amphibole, chlorite, calcite
156	Filtrate	+1.08	Aragonite, calcite, amorphous phase
230	Filtrate	+1.14	Aragonite, calcite, amorphous phase
299	Filtrate	+1.16	Aragonite, calcite, amorphous phase
368	Filtrate	+1.12	Aragonite, calcite, amorphous phase

Note: OC – other components (Si, Al, Fe, ... oxides)

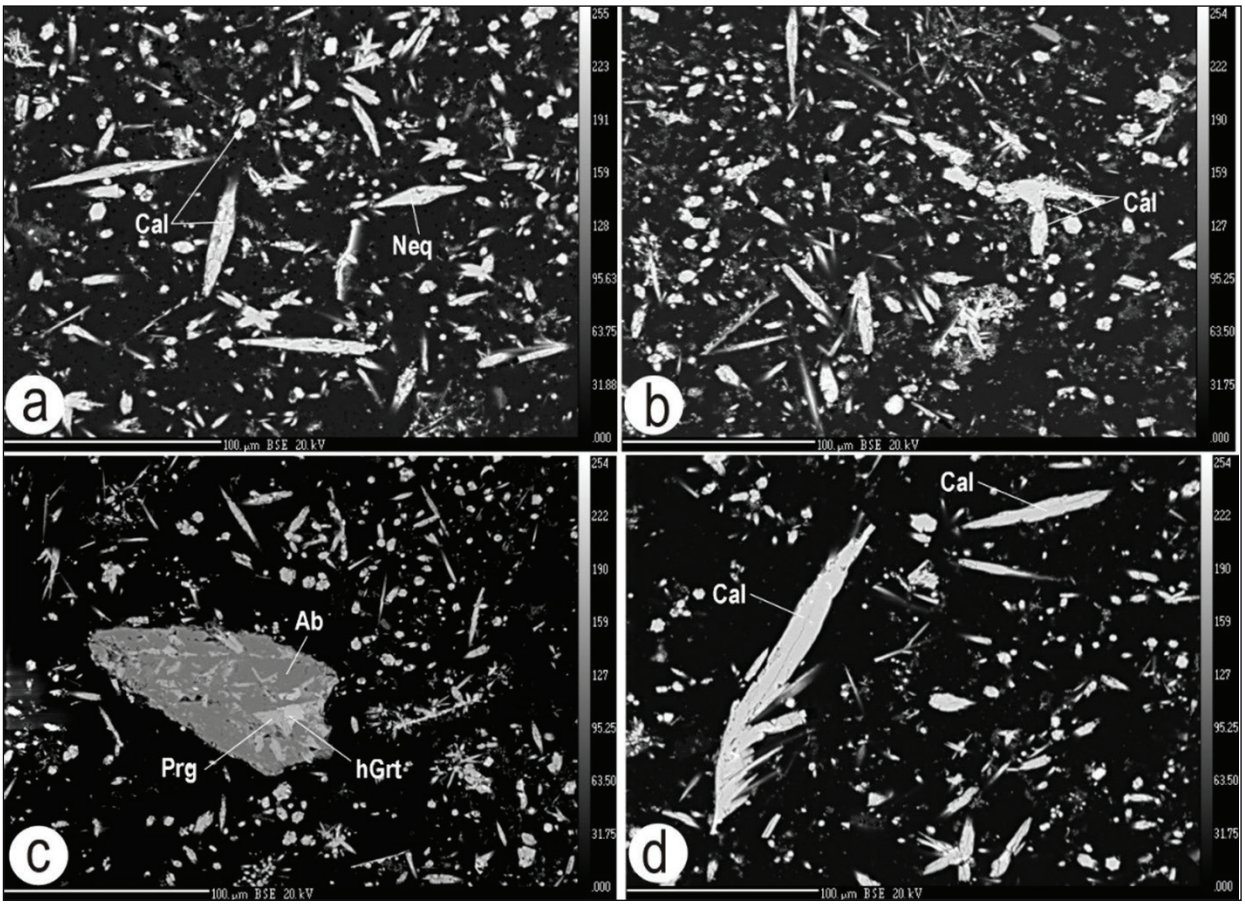

Fig. 14. Mineral composition of the carbonatization product of the metabasic rock **NK1.** Cal – calcite; Neq – nesquehonite. Crystallized filtrate **NK1** contains unreacted relics of albite (Ab), pargasite (Prg) and hydrated garnet (hGrt). BSE.

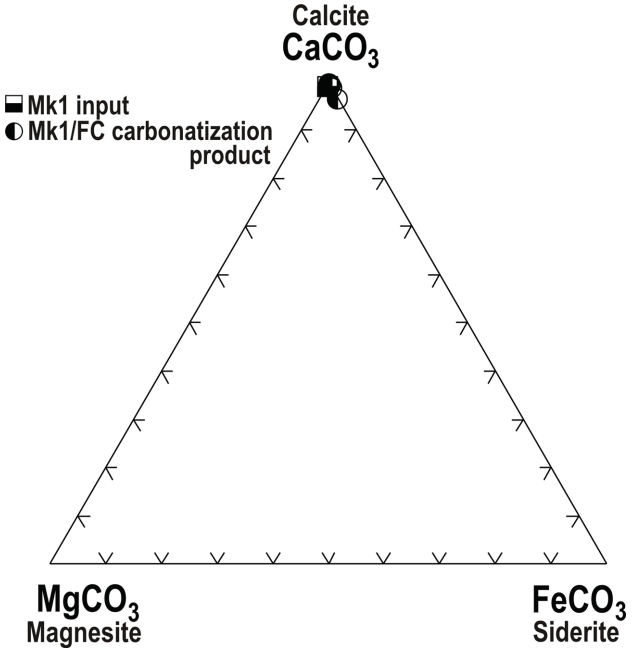

Fig. 15. Chemical classification of calcite and comparison of calcite in metabasic rock (input NK1) and calcite in the carbonatization product (NK1 – filtrate).

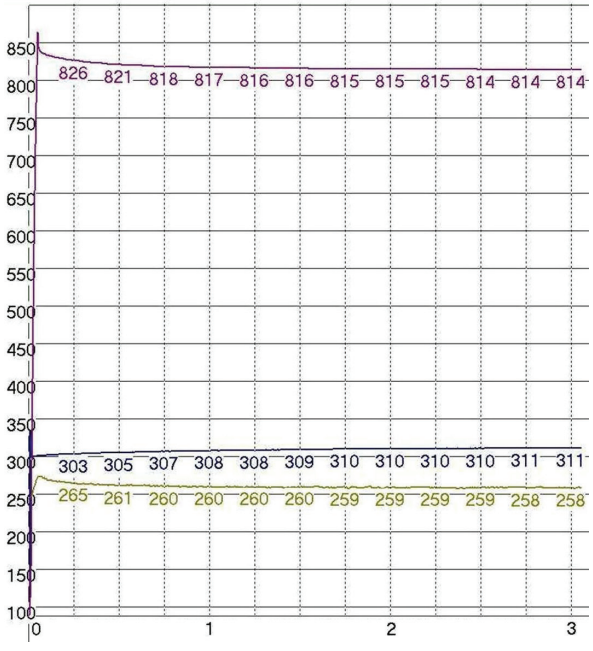

Fig. 16. Curve of pressure (psi, upper curve), stirrer rotation (rpm, middle curve) and temperature (°C, lower curve) during 3 hour carbonatization of the sample **NK1,** applying CO_2 with the purity 99.9 %.

The research in the case of metabasic rock NK1 found that the reaction of the "free" CaO and MgO from input minerals with CO_2 took place only to a minor extent due to their insufficient deliberation from the lattice of input minerals, despite that in the grist the grain-size beneath 20 μm formed nearly 50 %. The dried product from the filtrate contains 86.6 % $CaCO_3$ in the form of aragonite and calcite, binding 38.1 % of CO_2 (increase in comparison with the input is by 36.71 %).

In the case of total amorphization of input minerals (amphibole, chlorite, plagioclase) by sufficiently long milling, resulting in total lattice destruction of the minerals of **NK1** sample, resulting to full activation of Ca and Mg component for reaction with CO_2 and synthesizing $CaCO_3$ and hydromagnesite (100 % conversion), the 1 tonne of CO_2 will be bound by 9.806 tonnes of the sample NK1.

Chlorite schist from locality Gelnica (GE)

Chlorite schist **GE** from the locality Gelnica (Figs. 5a, b and 17a, b) represents the grey-green schistose pelitic rock with sandy and silty intercalations of grey colour and frequent ochre colouration (Fig. 18a). Phyllosilicates (chlorite, sericite) prevail in the mineral compositon. The sampled chlorite schists belong to Lower Paleozoic of Gemericum, Gelnica Group, Smolník Formation (cf. Grecula et al., 2009). Elongated outcrop of these rocks is located 250 m to WSW from railway station in the town of Gelnica. Coordinates: 49°51`24.43``N, 20°56`41.34``E. The sample of chlorite schist we took into the investigation due to its high content of FeO (4.46 wt.%) at low contents of CaO and MgO, and also owing our earlier findings that binding of CO_2 on FeO generates siderite (cf. Tuček et al., 2010).

Chlorite schists represents a dominating rock type in Gemericum. Usually they represent the tectonites of chlorite phyllite, which protolith was associated also with the extrusive volcanic material, resp. they represent diaftorites (mylonites) of other foliated rocks with dominating chlorite (Fig. 17c, d). The former Variscan deformation VD_1, caused by the WSW-vergent overthrust of exhumed Rakovec mélange in the hanging wall of the outcrop of sampled chlorite schist **GE,** is overprinted by the Alpine north-vergent imbrication in the deformation phase AD_1 and the strike-slips in the phase AD_3 (cf. Németh in Radvanec et al., 2007; Németh et al., 2012). Chlorite schists of the Smolník Formation (sensu Grecula et al., 2009) are present in tectonic unit Gemericum in several zones and represent very abundant lithological type.

The sample GE was prepared for reaction applying the same procedure as stated in previous samples. The input chemical and mineral compositions are available in Table 1. Investigated sample contained only one mineral (chlorite 16.6 %), binding in its structure Mg and Fe^{2+} components, potentially appropriate for binding CO_2 (Table 1). A small amount of CaO (0.16 %) is bound in calcite (0.3 %).

As seen from the Table 8, the input **GE** sample grist (Fig. 18a) with the grain-size <0.5 mm contains 54.57 % of the finest class (<0.02 mm), which represents more than half of the total amount. The carbonatization potential of the grist, expressed by the sum of Mg and Fe^{2+} oxides, is 6.05 %.

Carbonatization tests of the GE sample

The CO_2 reactivity tests with whole MgO and Fe^{2+} components of the sample GE were done in the high-pressure reactor at **five durations of reactions with CO_2** (1, 3, 6, 12 and 24 hours), **five input CO_2 pressures** (2, 4, 6, 8 and 10 MPa) and **four suspension densities** (156, 230, 297 and 368 g/l) at optimum stirrer rotations 400 rpm (Tab. 14).

In the case of reacting the whole amount of MgO (1.59 %) and FeO (4.46 %) with the origin of Mg and Fe carbonates, the maximum theoretical increase of the weight yield of the product after reaction with CO_2 would

Tab. 13
Chemical and mineral composition of divided carbonatization products of the sample **NK1** tests at reaction parameters: **22 °C, 6 MPa, 156 g/l, 400 rpm** and **3 hours reaction**

Chemical composition of **filtration cake – K** (wt.%)							
NK1	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2
+1.30 %	52.3	15.2	8.98	6.04	5.58	6.89	1.06
MnO	K_2O	Na_2O	P_2O_5	Cr_2O_3	SO_3	Ign. loss	CO_2
0.12	0.24	5.8	0.10	0.0007	<0.01	3.49	0.61
Chemical composition of the **product from filtrate – F** (wt.%)							
NK1	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2
+1.30 %	2.27	0.07	3.19	0.36	49.7	2.47	<0.01
MnO	K_2O	Na_2O	P_2O_5	Cr_2O_3	SO_3	Ign. loss	CO_2
0.31	0.11	<0.2	<0.01	0.0586	<0.01	41.8	38.1
Mineral composition of the **filtration cake – K** (wt.%)							
plagioclase		amphibole		chlorite		calcite	
Mineral composition of the **product from filtrate – F** (wt.%)							
aragonite + calcite		86.6		amorphous phase		13.4	

Note: AF – Amorphous phase formed by Si, Fe, ... oxides

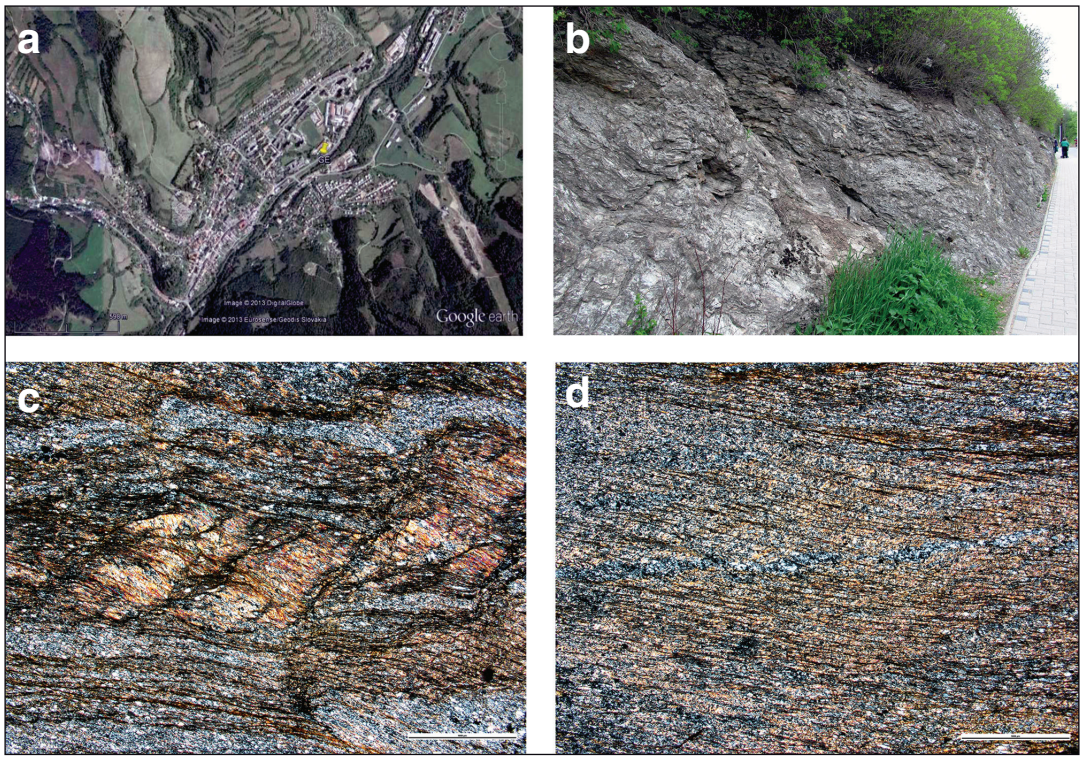

Fig. 17. The chlorite schist **GE** from the NE part of the Gelnica town (a) sampled in the elongated strongly tectonized rock outcrop (b), represents a strongly foliated rock (c, d), where the secondary foliation is segmenting the former bedding, consisting of alternating pelitic and psammitic beds. Plane polarized light, crossed nicols. Width of view 4.7 mm. Orthophotomap (a) is from Google Earth.

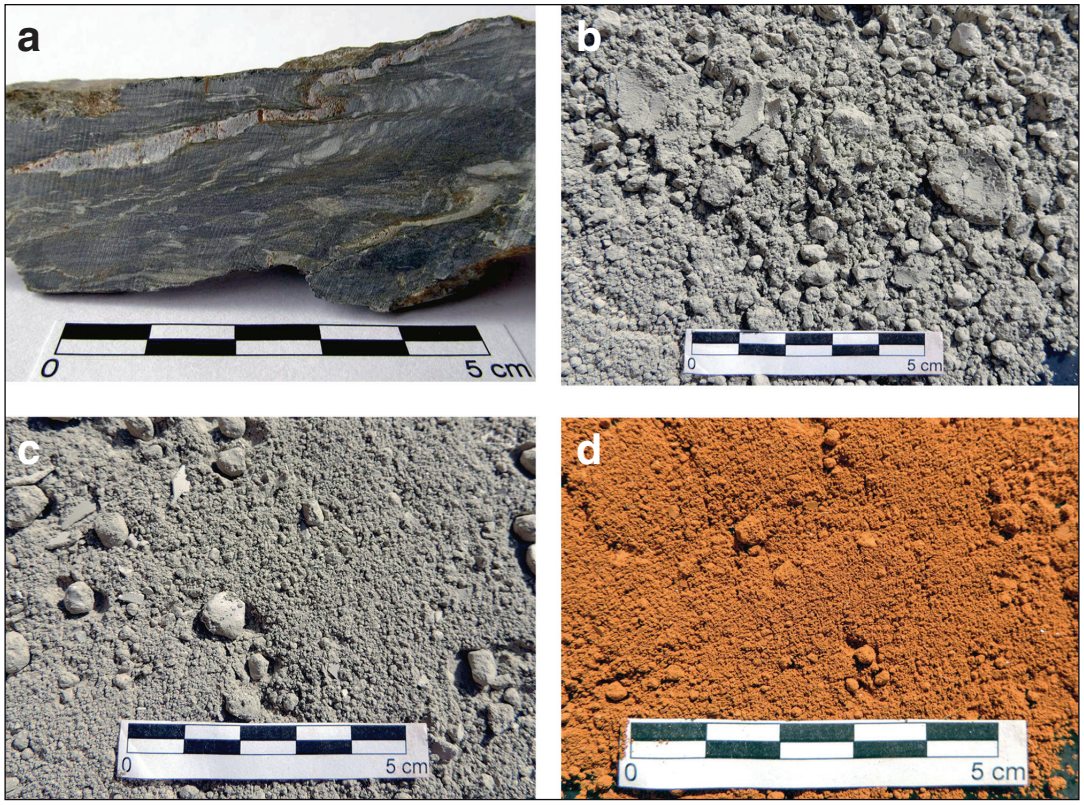

Fig. 18. Tested sample of the chlorite schist GE. **a** – hand-sample; **b** – input grist <0.5 mm; **c–d** – carbonatization products: c – filtration cake, d – filtrate.

represent an increase by +4.84 %, i.e. from 1 kg of the sample grist <0.5 mm there would originate 1.0484 kg of carbonatized product.

Artificial reaction of chlorite bearing schist with a mixture $H_2O + CO_2$ proceeds in limited extent according to reaction (5).

Reactions at differing durations of CO_2 reactions have demonstrated that the increases of the total weight yield of carbonatization products (Tab. 14) were low and were growing slightly in the range from +0.24 % to +0.80 % in duration from 1 to 24 hours. Dried filtrates contained precipitated calcite, manganocalcite and aragonite. The filtration cakes contained still all input minerals, because the Mg and Fe^{2+} components from chlorite practically did not react with CO_2 at given carbonatization conditions due to their insufficient deliberation from the lattice of this mineral.

At increasing pressures (2–10 MPa; Tab. 14) during 1 hour reaction the total increases of the weight yield were low (0.08 % to 0.20 %) with the origin of manganocalcite (kutnahorite) and aragonite besides some amount of amorphous phase. The filtration cakes were bearing the input minerals, including chlorite. The starting suspension temperature during the CO_2 pressure increase became higher and varied in the range 31–35 °C due to reaching the CO_2 critical state.

The increase of the suspension density (Tab. 14) caused the decrease of total amount of carbonatized product from +0.28 % to +0.15 %. The dried products from filtrates contained manganocalcite (kutnahorite) and amorphous phase (Fig. 19). The suspension density 156 g/l was proved to be sufficient.

As demonstrated in Tab. 14, the increase of the weight yield of carbonatized products is only around +0.08 % to +0.80 % (in average 0.44 %), which represents the value ca 11-times lower that the theoretically possible value (+4.84 %). The final test at the temperature **22 °C,** CO_2 pressure **6 MPa,** suspension density **156 g/l,** stirrer rotations **400 rpm** and reaction duration **3 hours,** applying the **GE** grists with the grain-size <0.5 mm with following suspension filtration has produced the filtration cake (Fig. 18c) and filtrate (Fig. 18d). The increase of the weight yield of this compound carbonatization product was +0.4 %. Its chemical and mineral compositions are summarized in Table 15.

As manifested in Fig. 21, during first 1–2 minutes of reaction with CO_2 (purity 99.9 vol.%) the suspension

$$\underset{\text{chlorite}}{(MgMnAl)_{12}(Al_2Si_6)_8O_{20}(OH)_{16}} + 6CO_2 + 3H_2O \rightarrow \underset{\text{kutnahorite}}{3MnMg(CO_3)_2} + \underset{\text{allophanite-amorphous phase}}{2Al_2O_3{\cdot}(SiO_2)_{1.3-3}{\cdot}(H_2O)_{2.5-3}} \quad (5)$$

Tab. 14
Carbonatization results of the grist of chlorite schists sample **GE,** applying reactions at temperature 22 °C, stirrer rotation **400 rpm** and differing durations of reactions, CO_2 pressure and density of suspension

Changed reaction parameter	Product	Total yield (wt.%)	Mineral composition (wt.%)
			PL – plagioclase; CHL – chlorite; QTZ – quartz; CC – calcite; MCA – mica; KFS – K-feldspar; AF – amorphous phase; OC – other components
GE	Input	–	PL 10.8; CHL 16.6; QTZ 20.2; MCA 47.0; KA 0.3; KFS 1.7; OC 3.4
Changed duration of reaction (1, 3, 6, 12, 24 hours) at pressure 6 MPa and suspension density 156 g/l			
	Cake	–	Quartz, chlorite, mica, plagioclase, K-feldspar
1	Filtrate	+0.24	Manganocalcite (kutnahorite), aragonite, amorphous phase
3	Filtrate	+0.24	Manganocalcite (kutnahorite), amorphous phase
6	Filtrate	+0.24	Manganocalcite (kutnahorite), amorphous phase
12	Filtrate	+0.44	Manganocalcite (kutnahorite), amorphous phase
24	Filtrate	+0.80	Calcite, manganocalcite (kutnahorite), aragonite, AF
Changed CO_2 pressures (2, 4, 6, 8, 10 MPa) at 1 hour lasting reactions and suspension density 156 g/l			
	Cake	–	Quartz, chlorite, mica, plagioclase, K-feldspar
2	Filtrate	+0.08	Manganocalcite (kutnahorite), aragonite, AF
4	Filtrate	+0.12	Manganocalcite (kutnahorite), aragonite, AF
6	Filtrate	+0.16	Manganocalcite (kutnahorite), aragonite, AF
8	Filtrate	+0.20	Manganocalcite (kutnahorite), aragonite, AF
10	Filtrate	+0.20	Manganocalcite (kutnahorite), aragonite, AF
Changed suspension density (156, 230, 297 and 368 g/l) at 1 hour lasting reactions and CO_2 pressures 6 MPa			
	Cake	–	Quartz, chlorite, mica, plagioclase, K-feldspar
156	Filtrate	+0.28	Manganocalcite (kutnahorite), amorphous phase
230	Filtrate	+0.19	Manganocalcite (kutnahorite), amorphous phase
297	Filtrate	+0.16	Manganocalcite (kutnahorite), amorphous phase
368	Filtrate	+0.15	Manganocalcite (kutnahorite), amorphous phase

Note: OC – other components (Si, Al, Fe, ... oxides), MCA – mica (sericite); AF – amorphous phase

temperature in reactor has increased from ca 22 °C to ca 27 °C due to indistinct exothermic reaction course. The decrease of the input CO_2 pressure during 3 hours is very slow, and from the 15. minute to 3 hours it has linear trend.

The research in the case of the GE sample has found that reaction of Mg and Fe^{2+} oxides from input chlorite with CO_2 has progressed in a very small extent due to their insufficient deliberation from the chlorite lattice despite the fact that in the grist the grain-size class <20 μm represented nearly 55 %. The dried product from filtrate contains 41.4 % of manganocalcite (+kutnahorite), with bound 18.2 % of CO_2 (increase in comparison with input by 18.04 %).

In the case of full amorphization of input minerals, preferably of chlorite, by sufficiently long milling of the sample GE, causing the total destruction of the lattice of this mineral, and by this way the full activation of Mg and Fe^{2+} components for reaction with CO_2 (100 % conversion) there would be necessary 24.258 tonnes of the GE sample for binding of 1 tonne of CO_2.

Pyroxenic andesite from Slanec locality (SL)

The sample **SL** of pyroxenic andesite (Fig. 23a) was taken from the active quarry at the village of Slanec (Fig. 22a). The pyroxenic andesite in this locality represents a part of the Neogene lava flows of andesite stratovolcano Hradisko (the Hradisko Formation; cf. Kaličiak et al., 1996).

In mineral composition of input sample there prevail mafic minerals (amphibole, pyroxene, chlorite), light minerals are represented with intermediate plagioclases

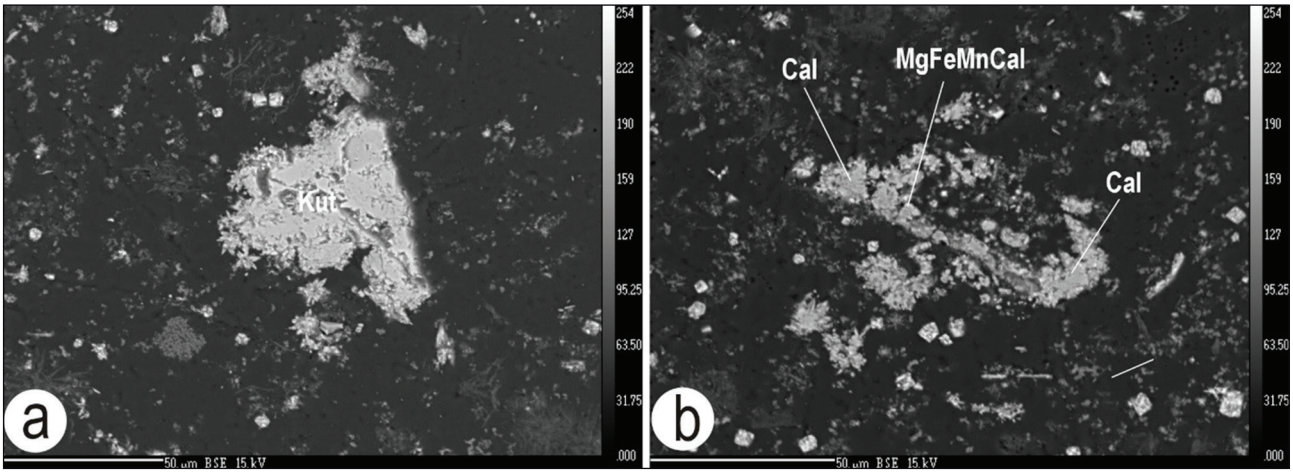

Fig. 19. Mineral composition of the product of artificial carbonatization of the chlorite schist GE (filtrate). Cal – calcite; Kut – kutnahorite; MgFeMnCal – MgFeMn calcite. BSE image.

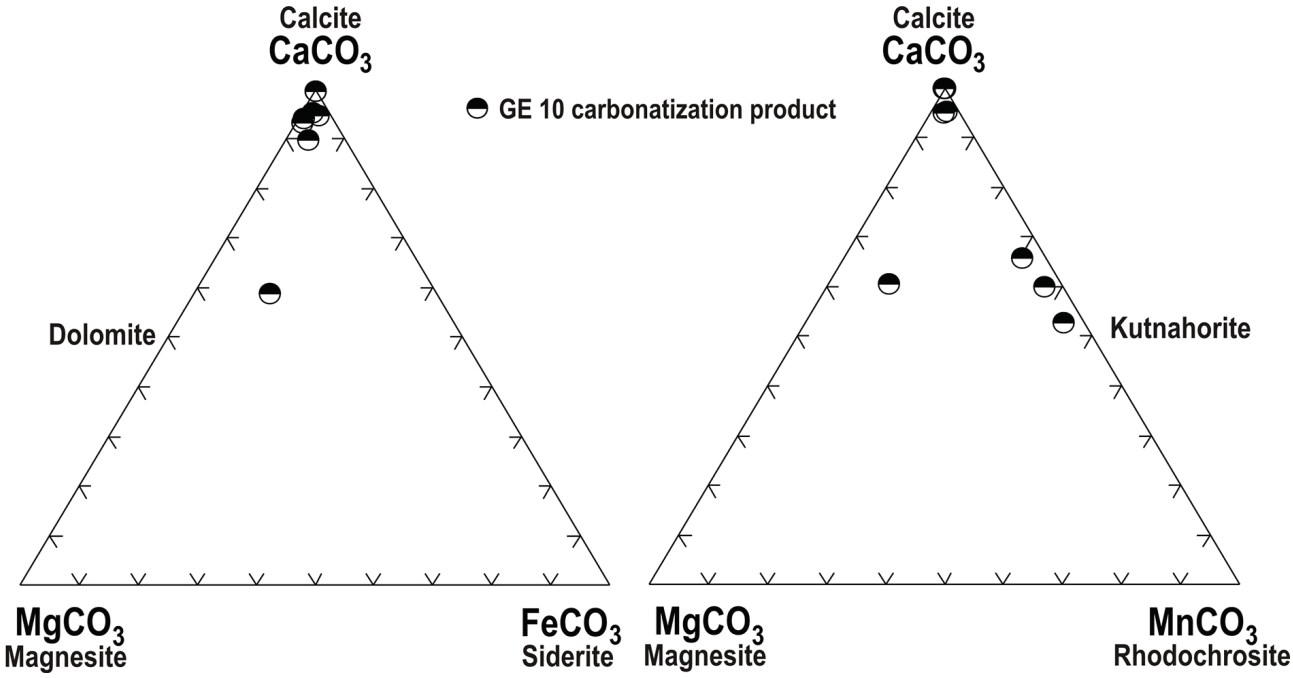

Fig. 20. Chemical classification of calcite, kutnahorite and dolomite, present in the artificial carbonatization product (filtrate) of the sample GE.

Tab. 15
Chemical and mineral composition of divided carbonatization products of the sample GE at following reaction parameters: **22 °C, 6 MPa, 156 g/l, 400 rpm** and **3 hours reaction**

Chemical composition of **filtration cake – K** (wt.%)							
GE	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2
+0.40 %	56.7	22.7	7.66	4.96	0.15	1.78	0.91
MnO	K_2O	Na_2O	P_2O_5	Cr_2O_3	SO_3	Ign. loss	CO_2
0.04	4.64	1.10	0.12	0.0136	<0.01	3.99	<0.01
Chemical composition of the **product from filtrate – F** (wt.%)							
GE	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2
+0.40 %	14.5	0.54	3.00	–	16.6	4.43	0.01
MnO	K_2O	Na_2O	P_2O_5	Cr_2O_3	SO_3	Ign. loss	CO_2
7.69	1.04	1.10	0.04	–	<0.01	23.9	18.2
Mineral composition of the **filtration cake – K** (wt.%)							
quartz		mica (sericite)		chlorite		plagioclase and K-feldspar	
Mineral composition of the **product from filtrate – F** (wt.%)							
manganocalcite (+KT)		41.4		amorphous phase		58.6	

Note: AF – amorphous phase formed by Si, Fe, ... oxides; KT – kutnahorite

and quartz (Tab. 1, Fig. 22b). Amorphous phase is represented with volcanic glass.

In this sample, the sources of Ca, Mg and Fe^{2+} components are these minerals: plagioclase (61.8 %), amorphic phase of non-stoichiometric composition (6.3 %) and futher minerals (6.2 %). Quartz (24.8 %) and calcite (0.9 %) are not appropriate for reaction with CO_2.

The sample **SL** underwent the same preparatory procedures as the samples GP, NK1 and GE. Its chemical and mineral composition is stated in Table 1 and grain-size composition in Table 8.

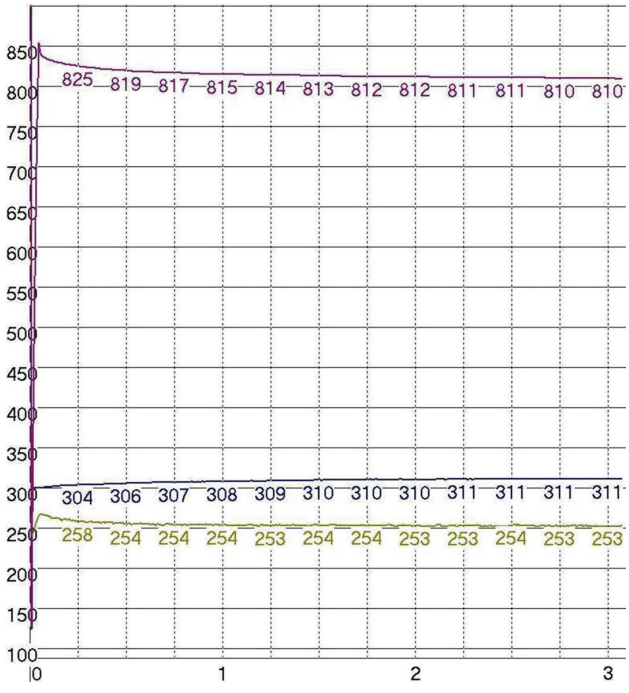

Fig. 21. Curve of pressure (psi, upper curve), stirrer rotation (rpm, middle curve) and temperature (°C, lower curve) during 3 hour carbonatization of the sample **NK1,** applying CO_2 with the purity 99.9 %.

A shown in Table 8, in the grist of the input sample SL with granularity <0.5 mm (Fig. 23b), the content of the finest grain-size class (<0.02 mm) is 34.91 %, which represents one third of the total amount of the sample. Concerning the efficiency of the reaction with CO_2, in sample is present prevailingly the dominating plagioclase (Tab. 1), binding in its structure Ca component. The Mg and Fe^{2+} components can be present also in amorphous phase and further non-specied phases. Futher present minerals like quartz and calcite do not provide appropriate chemical components for carbonatization reactions.

From above stated there follows that the SL sample grist (Fig. 23a) has a carbonatization potential, containing together up to 12.71 % of Ca, Mg and Fe^{2+} oxides, where from the input CaO content 7.71 % the "free" CaO represents 7.17 %.

Carbonatization tests of the SL sample grist

Correspondingly with previous samples, the SL sample carbonatization tests with "free" CaO and whole MgO, eventually Fe^{2+} components of the sample SL were performed in the high pressure reactor at **five durations of reactions with CO_2** (1, 3, 6, 12 and 24 hours), **five input CO_2 pressures** (2, 4, 6, 8 and 10 MPa) and **four suspension densities** (156, 230, 297 and 368 g/l; Tab. 16) at optimum stirrer rotations 400 rpm.

In the case of reacting of the whole share of MgO (2.73 %), FeO (2.80 %) and "free" CaO (7.17 %) from the input grist of the SL sample to Mg, Fe and Ca carbonates, the theoretical maximum increase of the weight yield of undivided carbonatization product would represent +10.94 %, i.e. from 1 kg of sample grist of the grain-size <0.5 mm there would originate 1.1094 kg of

carbonatized product. Tests aimed to reach this yield and to reduce or totally eliminate the plagioclase content in the carbonatization product.

The artificial carbonatization of andesite with a mixture $H_2O + CO_2$ proceeds in limited extent according to reaction (6).

The increases of the weight yields after carbonatization of the SL sample grist in the reactor (preferably of $CaCO_3$; Tab. 16) were low and varied in the range from +0.62 % to +0.84 % in duration of reaction from 1 to 24 hours. The highest increase was achieved after 1 hour (+0.84 %). At all durations of reactions the XRD analyses demonstrated the formation of aragonite + calcite in reaction products from filtrates. In filtration cakes there was identified also plagioclase, which substantial part of Ca component did not react with CO_2 at given carbonatization conditions even after 24 hours due to its insufficient deliberation of Ca from the plagioclase lattice.

As shown in Tab. 16, at input CO_2 pressure ≤6 MPa the total increase of the weight yield in the carbonatization product was 0.30–0.34 %, at pressures ≥8 MPa it was 0.52–0,66 %, though the reaching of supercritical CO_2 parameters (temperature above 31.1 °C and pressure above 7.39 MPa) is demanding from economic, time, as well as technical aspects. Concerning this fact and taking into account the results in Tab. 16, as appropriate CO_2 pressure we have determined the value 6 MPa. The carbonatization products (from filtrates) contained newly originated aragonite + calcite, and in the filtration cakes there was present plagioclase.

At all suspension densities (Tab. 16), the total increase of the weight yield of carbonatization product was low (from +0.20 to +0.48 %). The dried products from filtrates contained $CaCO_3$ in the form of aragonite and calcite. As sufficient suspension density we determined the value 230 g/l.

In all cases (Tab. 14) the increase of weight yields of undivided carbonatization products was low (from +0.20 to +0.84 %; in average +0.52 %), which means ca 20-times lower than theoretically possible (+10.94 %). The final test was carried out at following conditions: 22 °C, 6 MPa, 230 g/l, 400 rpm and 3 hours lasting reaction. After reaction, the increase of the weight yield of this carbonatization product was +0.6 %. The chemical and mineral composition of its divided carbonatization products are stated in Table 17 and shown in Figs. 23c, d; 24a, b and 25.

Correspondingly with previous lithological samples the exothermic trend of reaction is demonstrated with abrupt increase of the suspension temperature from ca 22 °C to ca 27 °C. Decrease of input CO_2 pressure is during 3 hours very slow, and after 15 minutes up to three hours it has a linear trend.

From above stated there follows that the reaction of the "free" CaO, MgO, event. FeO from the input grist with CO_2 proceeds only in small extent due to their insufficient deliberation from the lattice of their bearers, despite the grain-size <20 μm represented one third of its amount (34.91 %). In the dried product from the filtrate totally 86.6 % of $CaCO_3$ in the form of aragonite and calcite are present, binding 38.1 % of CO_2 (increase in comparison with input values by 36.71 %).

In the case of total amorphization of suitable input mineral components, prevailingly plagioclase by sufficiently long milling of the sample SL, when the total destruction of the mineral lattice takes part, resulting in full activation mainly of Ca, event. Mg and Fe^{2+} components for reaction with CO_2. If 100 % conversion occurs, the all "free" part of Ca component and whole amount of Mg and Fe^{2+} react with CO_2 with origin of $CaCO_3$, hydromagnesite and siderite. In such case 10.267 tonnes of the andesite of sample SL can bind 1 tonne of CO_2.

Summary of the carbonatization results of four lithological types

Comparing of four tested rock types (Table 1), it is obvious that all have a carbonatization potential expressed by the sum of Ca, Mg and Fe^{2+} oxides from 6.21 % **(GE)** to 24.69 % **(GP).** The input suspensions of the samples manifested a neutral reaction (pH ~ 6.5–7), besides the amorphized sample **GPA** with the suspension pH ~ 9,5.

Table 18 provides the final results of the four rock samples carbonatization in the high-pressure reactor. The best results of the rock samples were obtained by the sample **GP** with the subsequent amorphization of the talc and chlorite **(GPA),** where the Mg component from these minerals has reacted with CO_2 to hydromagnesite. At appropriate carbonatization conditions during three hours a new carbonate product has crystallized from the filtrate with the content of 86.6 % hydromagnesite, in which structure is fixed 32.6 % CO_2 with an increase of weight yield of the compound product +5.44 %. Table 18 further shows that for liquidation of 1 tonne of CO_2 by the methodology of carbonatization there is real need of 5.031 tonnes of material of the sample **GPA.** The sample suspension after carbonatization at conditions stated in Tab. 18 changed from pH 9.5 to 8.

The second positive sample **NK1** allowed to prepare after 3 hour carbonatization a new carbonate product with the $CaCO_3$ content 86,6 %, in which structure totally 38.1 % CO_2 was bound with the low increase of the weight yield of compound product +1.3 %. The liquidation of 1 tonne of CO_2 requires 9.806 tonnes of amorphized metabasic rock of the sample **NK1.** The sample suspension after carbonatization manifested pH around 7.5.

Third sample – andesite **SL** has provided a new carbonate product with 71.1 % $CaCO_3$, having bind in its lattice 31.3 % of CO_2 with very low increase of the weight yield of compound product +0.6 %. The liquidation of 1 tonne of CO_2 requires in this case 10.267 tonnes of amorphized material of the sample **SL.**

The worst carbonatization potential was found in the case of the chlorite schist sample **GE,** providing carbonate product with 41.4 % of manganocalcite (+kutnahorite).

$$\underset{\text{plagioclase}}{CaAl_2Si_3O_8} + CO_2 + 5H_2O \rightarrow \underset{\text{calcite}}{CaCO_3} + \underset{\text{allophanite-amorphous phase}}{Al_2O_3{\cdot}(SiO_2)_{1.3–3}{\cdot}(H_2O)_{2.5–3}} \quad (6)$$

Tab. 16
Carbonatization results of the grist of pyroxenic andesite sample **SL,** applying reactions at temperature **22 °C,** stirrer rotations **400 rpm** and differing durations of reactions, CO_2 pressure and density of suspension

Changed reaction parameter	Product	Total yield (wt.%)	Mineral composition (wt.%)
			PL – plagioclase; QTZ – quartz; CC – calcite; OC – other components; AF – amorphous phase
SL	Input	–	PL 61.8; QTZ 24.8; CC 0.9; OC 6.2; AF 6.3
	Cake	–	Plagioclase, quartz, amorphous phase
1	Filtrate	+0.84	Aragonite, calcite, AF, kutnahorite?
3	Filtrate	+0.80	Aragonite, calcite, AF, kutnahorite?
6	Filtrate	+0.80	Aragonite, calcite, AF, kutnahorite?
12	Filtrate	+0.62	Aragonite, calcite, AF, kutnahorite?
24	Filtrate	+0.74	Aragonite, calcite, AF, kutnahorite?
Changed CO_2 pressures (2, 4, 6, 8, 10 MPa) at 1 hour lasting reactions and suspension density 156 g/l			
	Cake	–	Plagioclase, quartz, amorphous phase
2	Filtrate	+0.34	Aragonite, calcite, AF, kutnahorite?
4	Filtrate	+0.32	Aragonite, calcite, AF, kutnahorite?
6	Filtrate	+0.30	Aragonite, calcite, AF, kutnahorite?
8	Filtrate	+0.52	Aragonite, calcite, AF, kutnahorite?
10	Filtrate	+0.66	Aragonite, calcite, AF, kutnahorite?
Changed suspension density (156, 230, 297 and 368 g/l) at 1 hour lasting reactions and CO_2 pressures 6 MPa			
	Cake	–	Plagioclase, quartz, amorphous phase
156	Filtrate	+0.24	Aragonite, calcite, AF, kutnahorite?
230	Filtrate	+0.48	Aragonite, calcite, AF, kutnahorite?
297	Filtrate	+0.31	Aragonite, calcite, AF, kutnahorite?
368	Filtrate	+0.20	Aragonite, calcite, AF, kutnahorite?

Note: OC – other components (Si, Al, Fe, ... oxides)

Tab. 17
Chemical and mineral composition of divided carbonatization products of the andesite sample **SL** obtained at carbonatization parameters: **22 °C, 6 MPa, 230 g/l, 400 rpm** and **3 hours** lasting reaction

Chemical composition of **filtration cake – K** (wt.%)							
SL	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2
+0.60 %	58.3	18.5	6.93	3.09	7.48	2.84	0.71
MnO	K_2O	Na_2O	P_2O_5	Cr_2O_3	SO_3	Ign. loss	CO_2
0.08	1.14	3.0	0.09	0.0020	0.23	0.52	<0.01
Chemical composition of the **product from filtrate – F** (wt.%)							
SL	SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	TiO_2
+0.60 %	5.35	0.22	8.66	0.72	40.5	5.73	<0.01
MnO	K_2O	Na_2O	P_2O_5	Cr_2O_3	SO_3	Ign. loss	CO_2
1.56	0.11	0.3	<0.01	0.0979	1.61	36.0	31.3
Mineral composition of the **filtration cake – K** (wt.%)							
plagioclase		quartz		amorphous phase		other unspecified components	
Mineral composition of the **product from filtrate – F** (wt.%)							
aragonite + calcite		71.1		amorphous phase		28.9	

Note: AF – amorphous phase formed by Si, Fe, ... oxides

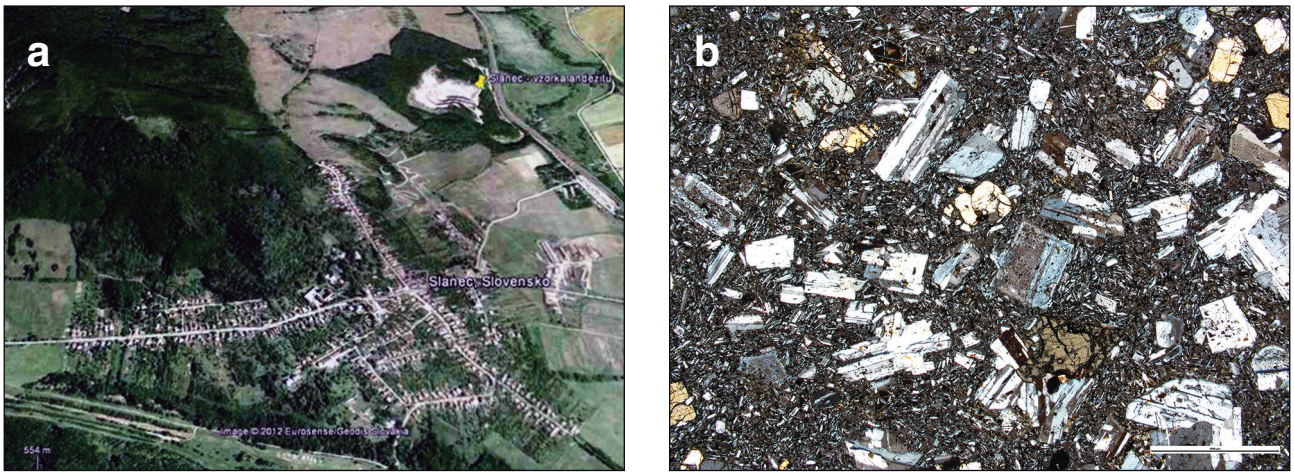

Fig. 22. a – Location of the pyroxenic andesite quarry (sampling site of the SL sample) ca 500 m NNE of the Slanec village center; **b** – Microphotograph of studied pyroxenic andesite with dominating pyroxene, plagioclase and olivine phenocrysts in the fine-grained matrix. Width of view 4.6 mm. Orthophotomap (a) is from Google Earth.

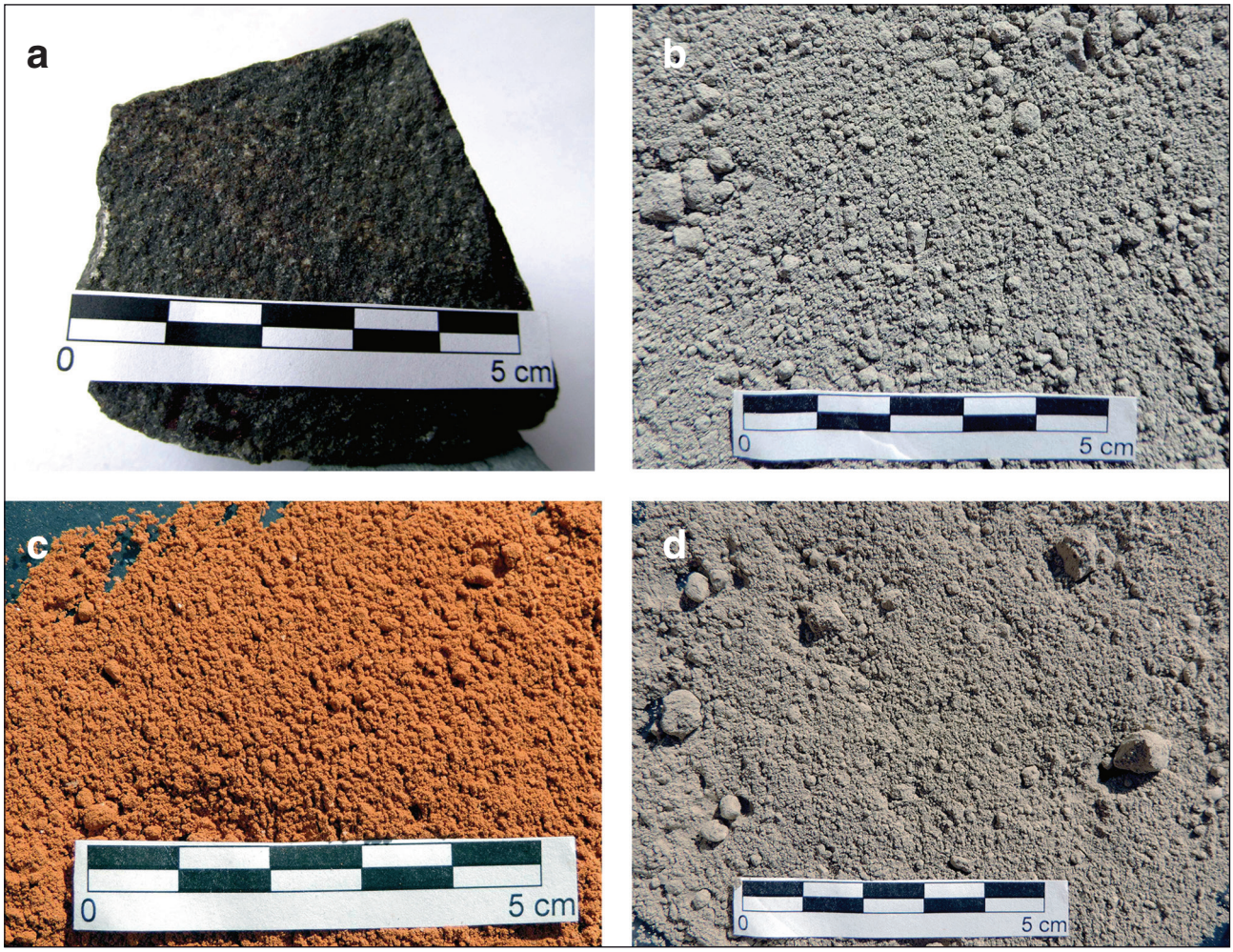

Fig. 23. Pyroxenic andesite SL: **a** – rock-sample; **b** – input grist <0.5 mm; **c –** filtrate after carbonatization; **d** – filtration cake.

In their lattices 18.2 % of CO_2 was bound with very low increase of the weight yield of compound product +0.4 %. The liquidation of 1 tonne of CO_2 by the chlorite schists of the sample GE type requires 24.258 tonnes of amorphized material of the sample **GE.**

The necessary chemical compounds of appropriate input minerals in tested rock types can be deliberated by intensive milling, reaching their amorphization, but it is unviable due to the huge quantities of necessary rocks for liquidation of 1 tonne of CO_2 – from 5.031 tonnes **(GPA)** up to 24.258 tonnes **(GE).**

Conclusions

The possibilities of permanent liquidation of CO_2 by artificial carbonatization were tested applying one industrial waste (chromium-magnesium brick) sample, and four rock samples. Their carbonatization conditions are stated in Table 19. Tested materials contain minerals with Ca, Mg, resp. Fe^{2+} components, which at appropriate temperature--pressure-time conditions are suitable to liquidate CO_2 binding it to lattice of newly formed carbonates.

In the case of the sample of chromium-magnesium waste **(MT)** the sum of CaO, MgO and FeO components is up to ca 81 %. In rock samples the sum of Ca, Mg and Fe^{2+} oxides was in the range from ca 6 % **(GE)** up to ca 25 % **(GP):** GP – 22.4 % MgO, NK1 – 7.57 % MgO, GE – 4.46 % FeO and SL – 7.71 % CaO (Tab. 1). Mg component was present prevailingly in talc **(GP)** and chlorite **(GP, NK1, GE),** Ca component prevailingly in plagioclase **(NK1, SL)** and Fe^{2+}, resp. Ca component prevailingly in amphibole structure **(NK1).**

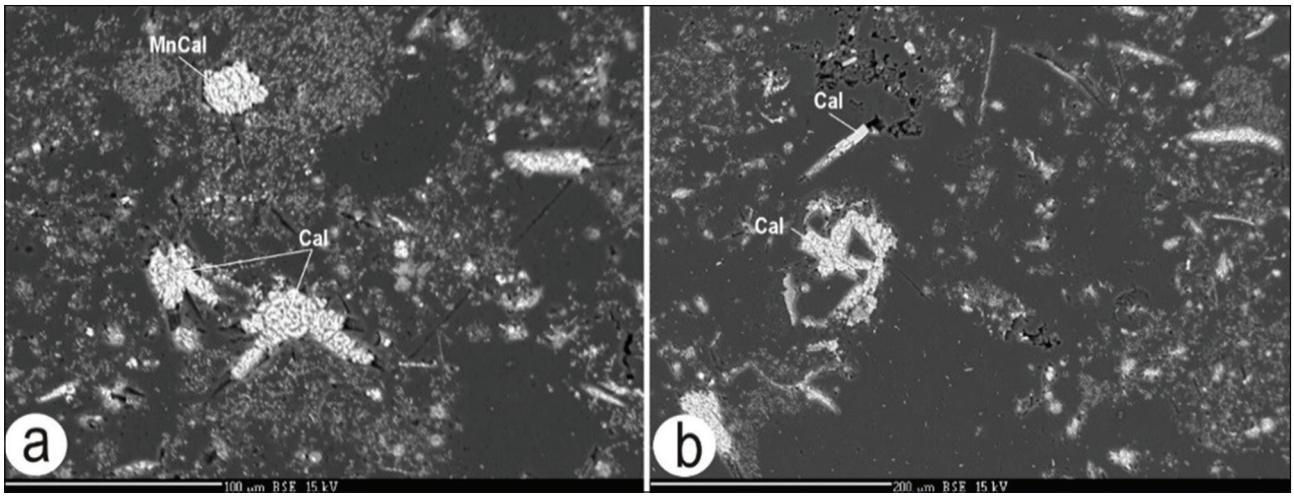

Fig. 24. a–b – Mineral composition of the andesite sample SL artificial carbonatization product. Cal – calcite; Dol – dolomite; MnCal – Mn calcite. BSE image.

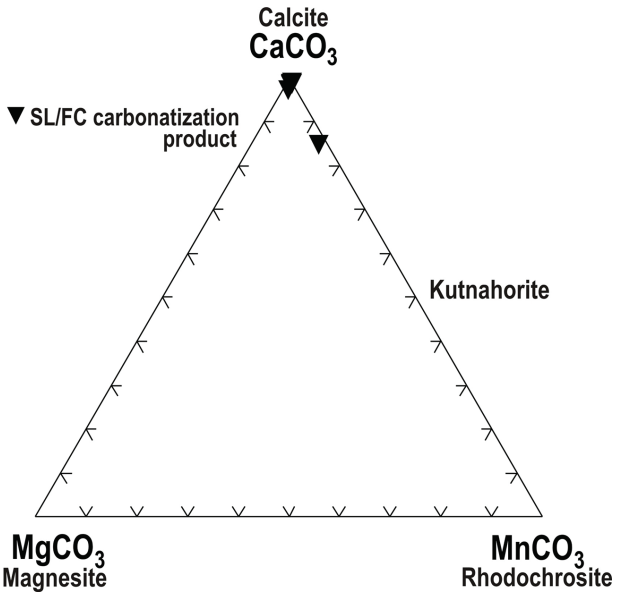

Fig. 25. Chemical classification of calcite and Mn calcite, being the products of artificial carbonatization of the andesite sample SL.

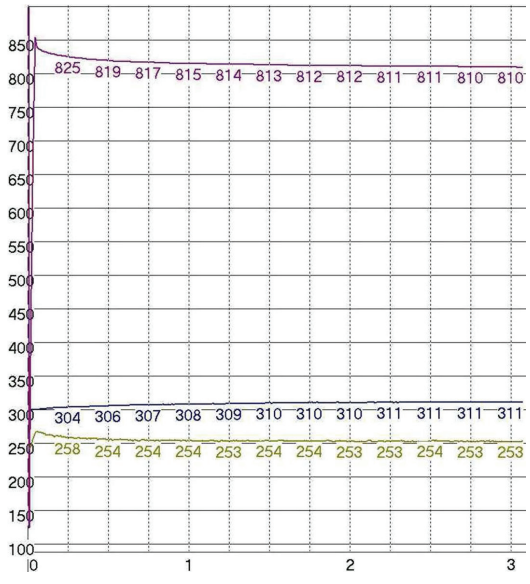

Fig. 26. Curve of pressure (psi, upper curve), stirrer rotation (rpm, middle curve) and temperature (°C, lower curve) during 3 hour carbonatization of the sample **SL,** applying CO_2 with the purity 99.9 %.

The **MT** sample has a high carbonatization potential (Tab. 19), being expressed by a high content of MgO (78.3 %). The strongly alkaline reaction of input suspension of the sample MT (pH ~ 9.5 to 11.0) was lowered by the reaction to pH ~ 7.5.

In the waste sample **MT** with the Mg component from input reacted with CO_2 to hydromagnesite with relatively high conversion rate – 83.2 %, and a new carbonate product with contents of 73.5 % of hydromagnesite and 1.1 % of $CaCO_3$ (together 74.6 %), can bound 28.2 % of CO_2. **For liquidation of 1 tonne of CO_2 there is a need of 1.757 tonne of MT sample material,** which is the better result than was obtained at previous research applying serpentinite (metaperidotite) rock (Radvanec et al., 2008, 2013; Tuček et al., 2013). The positive fact is that the sample suspension after carbonatization had pH ~ 7.5. When comparing these result with those of tested rocks **GP, NK1, GE** and **SL** (Tab. 18), all samples have certain carbonatization potential, though worse than in the case of waste sample **MT.**

Conclusion and suggestions

The most significant contribution of tested methodology is the revealing and defining the optimum carbonatization conditions in the case of **MT** sample and proving of crystallization of new carbonates in the case of samples **GP, NK1, GE** and **SL,** leading to stable liquidation of CO_2 by artificial carbonatization, applying the **industrial waste as well as the natural materials** in laboratory conditions. After carbonatization, CO_2 remains permanently and safely bound in new products, in which the newly formed carbonates (prevailingly hydromagnesite, calcite and aragonite) thermodynamically stabilize CO_2 and allow its permanent deposition. Concerning the input materials for carbonatization, these should be inexpensive, and their

Tab. 18
Summary of carbonatization results of the samples of four rock types

Locality	Gemerská Poloma	Nižný Klátov	Gelnica	Slanec
Sample designation	**GP (GPA*)**	**NK1**	**GE**	**SL**
Lithotype	Talc-chlorite schist	Metabasic rock	Chlorite schist	Pyroxenic andesite
Minerals appropriate for carbonatization	Talc, chlorite	Amphibole, chlorite, plagioclase	Chlorite	Plagioclase, Mg-Ca amorphous phase
pH of suspension – input	~7 (~9.5*)	~7	~6.5	~7
CaO total content (%)	0.39	6.33	0.16	7.71
Content of free CaO (%)	0.39	4.56	0.16	7.17
MgO total content (%)	22.40	7.57	1.59	2.73
FeO content (%)	1.90	5.82	4.46	2.80
Maximum theoretical increase of undivided carbonatization products	+29.90 %	+13.60 %	+4.84 %	+10.94 %
Real increase of undivided carbonatization product – proved conditions	+5.44 %*	+1.30 %	+0.40 %	+0.60 %
Theoretical amount of sample material (t) per 1 t of CO_2	5.031*	9.806	24.258	10.267
Grain-size of input	beneath 0.5 mm	beneath 0.5 mm	beneath 0.5 mm	beneath 0.5 mm
Input CO_2 pressure (MPa)	6	6	6	6
Duration of reaction with CO_2 (hour)	3	3	3	3
Temperature of suspension (°C)	22	22	22	22
Stirrer rotation (rpm)	400	400	400	400
Suspension density (g/l)	156	156	156	230
pH of suspension after carbonatization	~7 (~8*)	~7.5	~6.5	~7
$CaCO_3$ content (wt.%)	–	86.6	41.4	71.1
Hydromagnesite content (wt.%)	86.6*	–	–	–
Content of all carbonates (wt.%)	86.6*	86.6	41.4**	71.1
CO_2 content (wt.%)	32.6*	38.1	18.2	31.3
Increase of CO_2 content in comparison with input (wt.% and multiplication)	+32.53* 465.7 x*	+36.71 27.4 x	+18.04 113.8 x	+36.71 74.5 x

Note: *Amorphous state of the grist of sample GP (GPA) was reached by milling; **manganocalcite (+kutnahorite)

source should be present closely to the facility producing CO_2 emissions (metallurgical plant, power plant, etc.). Positive is also revealing the exothermic character of the reaction with CO_2, so the heat produced by carbonatization reaction can be meaningfully used.

The **MT** grist suspensions had before carbonatization highly alkaline reaction – pH around 9.5–11, but carbonatization lowered this value to 7.5 (standard waste). Study of the hydromagnesite thermic stability has demonstrated that hydromagnesite is safe and stable medium for deposition of CO_2 in temperatures up to 300 °C (Teir, 2008). The products prepared from the MT waste sample contained ca 75 % of hydromagnesite. Simultaneously the precipitated hydromagnesite can be used e.g. as a semi-product for the production of chemically pure Mg compounds, as well the inorganic white filling to colours, paper, cements, and potentially it can be used also in other industrial branches like rubber industry, cosmetics and pharmacy (medicaments).

Table 19 comprendiously states the conditions of mineral sequestration of CO_2 at final demonstrative tests applying **rock samples GP, NK1, GE** and **SL:** grain-size <0.5 mm, input CO_2 pressure 6 MPa, duration of reaction 3.0 hours, temperature of suspension 22 ˚C, stirrer rotation 400 rpm and suspension density 156 to 230 g/l. New Ca (Mn)--Mg carbonatization products of the rock samples with carbonates contents 41.4–86.6 % had in their structure fixed 18.2–38.1 % CO_2. The conversions of given oxides due to their input into the lattice of carbonate minerals were very low, which is documented also by very low increase of the weight yield of products 0.40–5.44 % (for the sample of chromium-magnesium waste it was 69.28 %). For the process of CO_2 sequestration it is really necessary to apply **5.031–24.258 tonnes** of tested four rocks with input minerals in amorphous state for 1 tonne of CO_2, which is, concerning the expense for the whole process of mineral sequestration of CO_2 uneconomic. Suspensions of samples after the carbonatization have manifested pH around 6.5 to 8.

The above presented results we suggest in the future research (mainly for waste materials):

– use the carbonatization method for resolving the deposition of waste materials with harmful parameters, changing their physical-chemical parameters (e.g. asbestos-cement waste, waste after the thermic modification of carbonatic raw materials, etc.) applying internationally accepted test TCLP (toxicity characteristics leaching procedure), including the detection of their amounts, production and use in recycling processes;

– from the viewpoint of urgent problem related to the lack of some critical raw materials in European Union there is possible to use the carbonatization method mainly of the waste materials for preparation of enriched products usable in various industrial branches (saving of raw material sources) according to lately defined CCU (Carbon Capture utilization) conception, i.e. using the CO_2 mineral sequestration for preparation of new products;

– regarding the unreacted remains (solid remnants after

Tab. 19
Carbonatization at optimum conditions (**MT** sample) and tests for providing newly crystallized carbonates, products of carbonatization reaction with CO_2 in the case of four lithological samples (**GP, NK1, GE** and **SL**)

Locality	Jelšava	Gemerská Poloma	Nižný Klátov	Gelnica	Slanec
Sample designation	**MT**	**GP (GPA*)**	**NK1**	**GE**	**SL**
pH of suspension – input	~10	~7 (~9.5*)	~7	~6.5	~7
CaO+MgO content (%)	80.39	22.79	13.90	1.75	10.44
Free CaO content (%)	1.67	0.39	4.56	0.16	7.17
FeO content (%)	–	1.90	5.82	4.46	2.80
Real increase of carbonatic product	+69.28 %	+5.44 %*	+1.30 %	+0.40 %	+0.60 %
Theoretical amount of sample t/1 t CO_2	1.757	5.031*	9.806	24.258	10.267
Conversion of Ca, Mg, Fe^{2+} component	83.2 %	–	–	–	–
Optimum conditions of CO_2 mineral sequestration (carbonatization) applying the high-pressure reactor					
Grain-size of input material	below 0.1 mm	below 0.5 mm	below 0.5 mm	below 0.5 mm	below 0.5 mm
Input pressure CO_2 (MPa)	7	6	6	6	6
Duration of reactions with CO_2 (hour)	2.0	3.0	3.0	3.0	3.0
Suspension temperature (°C)	22	22	22	22	22
Stirrer rotation (rpm)	400	400	400	400	400
Suspension density (g/l)	159	156	156	156	230
Final carbonatized products					
pH of suspension after carbonatization	~7.5	~7 (~8**)	~7.5	~6.5	~7
Total content of carbonates (wt.%)	**74.6***	86.6**	86.6	41.4***	71.1
Content of CO_2 (wt.%)	**28.2***	32.6**	38.1	18.2	31.3

Note: ***joint carbonate products;** **intensive milling of the sample GP produced amorphous material (GPA); ***manganocalcite (+kutnahorite)

the waste carbonatization), there is necessary to monitor such elements in remains that are supposed as critical according to EU classification and focus further activities on methodology of their obtaining from appropriate remains after the waste carbonatization.

Finally we can conclude that use of the results of CO_2 sequestration by carbonatization can in the future contribute to four positive results for the environment and economy:

(1) lowering the amount of industrial CO_2 emitted to atmosphere, (2) lowering amounts and change of parameters of waste materials, (3) saving raw material sources for preparation of products usable in industry and (4) effective protection of the environment.

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