

CO₂ sequestration by carbonatization: Origin of new stable products using serpentinite and their potential use in industry

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Abstract. Article presents several methods of CO₂ sequestration with the main emphasis on mineral carbonatization. The main principles of this way of liquidation of industrial CO₂ – direct and indirect method of carbonatization are described with stating of general factors influencing the acceleration of carbonatization.

The carbonatization for CO₂ liquidation was tested using serpentinite from localities Rudník, Hodkovce and Jasov in Slovakia. The laboratory pilot tests have demonstrated that new, solid and high purity products of carbonatization can be prepared from samples of these localities after their granular and thermic modification at particular P-T conditions with subsequent crystallization of carbonate minerals from filtrates.

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

Key words: serpentinite, carbonatization, CO₂, P-T conditions, filtrate, crystallization, carbonates

1. Introduction

Sequestration of CO₂ is defined as catchment, deposition and storage of CO₂. It can be done by physical method (e.g. geological storing), chemical method (e.g. mineral carbonatization) and biological method (e.g. reforestation – photosynthesis of chlorophyll of green parts of the plants with CO₂).

CO₂ sequestration by mineral carbonatization represents safe method for liquidation of industrial CO₂, based on chemical reactions of active components of rocks, resp. waste, with CO₂, resulting in origin of stable and solid products - carbonates, eventually further inert compounds not loading living environment.

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

The carbonatization can be done by two methods – direct and indirect. Using the direct (one-phase) method the mineral components are added into reaction with CO₂. In indirect method (two-phase) the reactive components are extracted from mineral matrix and successively enter into the reaction with CO₂. In both cases the input minerals

can be modified by thermic, chemical, physical-mechanic or mutually combined ways aiming to accelerate the reactions with CO₂ (Uliasz-Bochenczyk et al., 2007).

Carbonatization (mainly the direct method) represents in normal natural conditions very slow process, mainly in the case of natural minerals. Aiming to accelerate the reactions, following factors influencing the reactivity of mineral components with CO₂ must be optimized technologically:

- a) mineral and chemical composition of input rocks (raw material) and activity of their components, purity of CO₂-bearing gas
- b) state of input components (solid, liquid and gas phase) and their mutual ratio
- c) temperature (T)
- d) pressure CO₂ (P)
- e) duration (time) of reaction – time of mutual reacting of solid phase with CO₂ (τ)
- f) grain-size (fineness), porosity and activity of specific surface of input material
- g) modification of input components (thermic, chemical, physical-mechanical, eventually their mutual combination)
- h) reaction conditions (static or dynamic)
- i) pH of reaction environment and kinds of added reactants (additives, reagents, etc.)
- j) density, resp. viscosity of reagent suspension

2. Carbonatization of serpentinite

The laboratory investigation was focused on 5 samples from Slovak localities: Hodkovce (HO-1 and HO-2),

Jasov (JA-1) and Rudník (RU-1 and RU-2). Samples were crushed in several steps, homogenized and quartered for chemical silicate analyses (CHA), X-ray diffraction analyses (RTG), differential thermic analyses (DTA) and differential thermogravimetric analyses (DTG).

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

Tab. 1. Chemical composition of input samples

Chemical compound (wt.%)	RU - 1	RU - 2	HO - 1	HO - 2	JA - 1
SiO ₂	37.87	39.62	40.21	40.01	40.61
Al ₂ O ₃	2.02	1.71	0.94	0.77	2.46
Fe ₂ O _{3 total}	6.15	6.36	7.27	8.04	5.74
FeO	0.22	0.11	0.15	0.11	1.09
CaO	4.44	2.02	0.72	0.24	2.61
MgO	34.75	36.47	36.06	36.73	36.23
TiO ₂	0.06	0.05	0.02	0.05	0.06
MnO	0.11	0.07	0.08	0.07	0.15
K ₂ O	<0.01	<0.01	<0.01	0.02	0.01
Na ₂ O	0.01	<0.01	<0.01	<0.01	0.06
P ₂ O ₅	0.01	<0.01	<0.01	0.01	<0.01
Cr ₂ O ₃	0.364	0.355	0.298	0.334	0.363
loss by ignition	13.98	13.03	14.12	13.44	11.41

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

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

The pilot test of samples were done at determined P-T conditions in laboratory rotating reactor with uninterrupted mixing of suspension formed by solid phase - serpentinite and liquid phase - water, with added CO₂. The ratio of solid phase to liquid phase was 1:5. The duration of carbonatization reactions was within the range 5-20 hours at room temperature and CO₂ pressures 0.1-0.3 MPa.

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

New, highly pure mineral phases crystallized from filtrates at temperatures 50 °C, 160 °C and 200 °C after

4-24 hours. Among these phases prevailed nesquehonite and hydromagnesite, less abundant were barringtonite, dypingite. In small amount there occurred also magnesite, dolomite and calcite grains (Radvanec et al., 2009).

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

3. Results of laboratory tests

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

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

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

DTA record of nesquehonite product obtained from the sample HO-2 at 50 °C shows double endoeffect with peaks at 182 °C and 209 °C being accompanied with the loss by ignition 34.9 %, double endoeffect with peaks at 428 °C and 478 °C with loss by ignition 31.3%. Comparison of DTA results with those from chemical analysis has demonstrated that weight loss with peak at 182-209 °C corresponds to loss of adsorption water - 3 H₂O. The weight loss at 428-478 °C corresponds to loss of the functional group - CO₂.

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

Comparison of DTA results with the results of chemical analysis has shown that endoeffect with the temperature peak at 321 °C corresponds with the loss of 19 % bounded water in the form of OH groups and own adsorption water - 4H₂O. The loss of weight 35.6 % with the peaks of endoeffect at 433 °C and 481-520 °C corresponds with the loss of functional group - CO₂.

4. Conclusion

Serpentinites from localities Rudník, Hodkovce and Jasov in Slovakia can be used for liquidation of industrial CO₂ using the method of carbonatization. The laboratory investigation has manifested that after the granular and

thermic modification of samples from investigated localities Rudník, Hodkovce and Jasov in Slovakia at certain P-T conditions the qualitatively new, solid and highly pure products can be prepared by the method of carbonatization with subsequent crystallization of carbonate minerals from filtrates.

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

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

The originated carbonate products with steady chemical bounds of CO₂ consisted mainly from nesquehonite, hydromagnesite and less barringtonite, dypingite as well as tiny magnesite, dolomite and calcium grains.

Tab. 2. Mineral composition of input samples

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

Tab. 3. Chemical composition of obtained products

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

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

Tab. 4. Mineral composition of obtained products

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

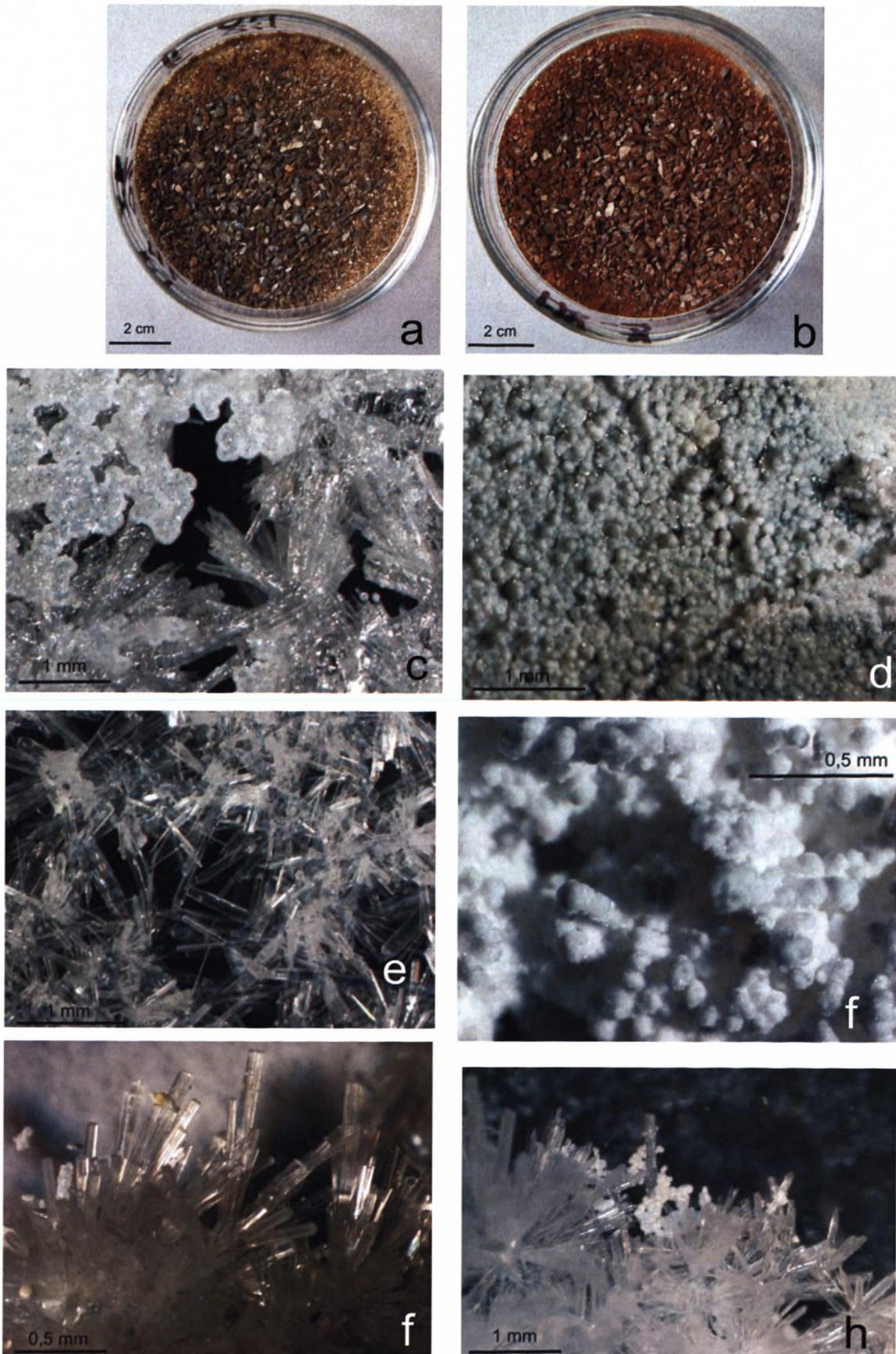


Fig. 1. Mineral sequestration of samples from Hodkovce and Rudnik localities. Sample Hodkovce 2: a - input material crushed beneath 1.0 mm, b - thermally elaborated material crushed beneath 1.0 mm, c - nesquehonite and hydromagnesite (160 °C), d - hydromagnesite (200 °C). Sample Hodkovce 1: e - nesquehonite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

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

Hodkovce 2 – Nesquehonite (50 °C)					
No.	Measured values			Etalon values	
	Angle	d(nm)	I	d (nm)	I
1	13.750	0.644	100.00	0.648	100.00
2	23.210	0.383	85.57	0.385	75.00
3	24.940	0.357	7.23	0.359	8.00
4	27.670	0.322	11.61	0.323	20.00
5	29.600	0.302	13.34	0.303	30.00
6	30.140	0.296	1.97	0.298	6.00
7	32.340	0.277	3.39	0.278	10.00
8	34.320	0.261	3.31	0.261	55.00
9	35.920	0.250	25.54	0.251	6.00
10	41.650	0.217	12.58	0.218	2.00
11	42.000	0.215	4.92	0.216	4.00
12	45.000	0.201	4.60	0.202	8.00
13	47.320	0.192	22.02	0.193	16.00

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

Hodkovce 2 - Hydromagnesite (200 °C)					
No.	Measured values			Etalon values	
	Angle	d(nm)	I	d (nm)	I
1	9.580	0.923	53.89	0.918	40.00
2	13.800	0.642	31.70	0.644	40.00
3	15.250	0.581	100.00	0.579	100.00
4	19.850	0.447	22.40	0.447	20.00
5	21.190	0.419	41.49	0.421	20.00
6	21.980	0.404	18.44	0.405	5.00
7	23.260	0.382	16.71	0.381	10.00
8	25.390	0.351	19.09	0.350	10.00
9	26.850	0.332	23.63	0.331	30.00
10	28.120	0.317	25.57	0.315	5.00
11	28.780	0.310	26.87	0.309	5.00
12	30.780	0.290	63.76	0.290	90.00
13	33.180	0.270	26.72	0.269	30.00
14	35.920	0.250	26.22	0.250	30.00
15	38.320	0.235	17.50	0.235	5.00
16	39.100	0.230	25.07	0.230	30.00
17	40.990	0.220	27.37	0.220	10.00
18	41.780	0.216	32.99	0.215	50.00
19	45.500	0.199	22.33	0.199	20.00

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

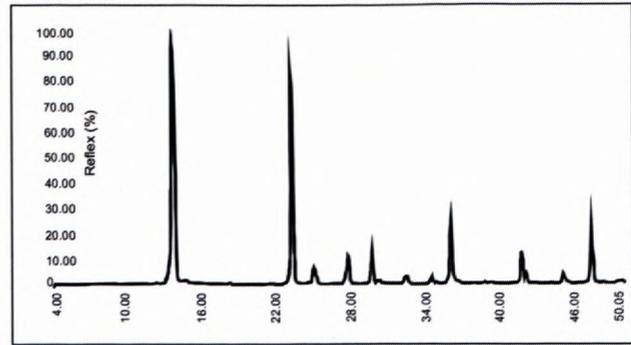


Fig. 2. X-ray diffraction record of nesquehonite (50 °C) from locality Hodkovce 2.

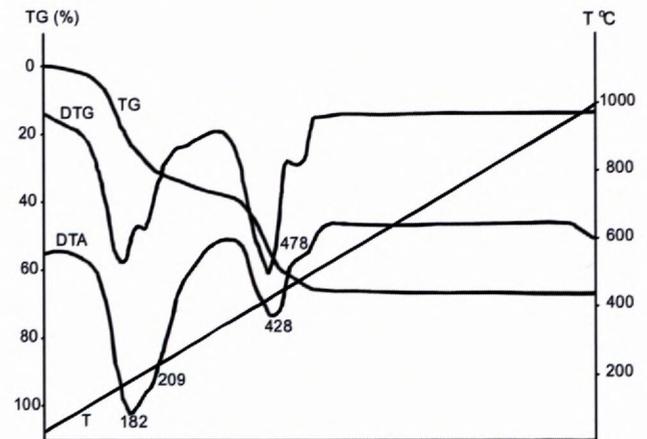


Fig. 3. DTA record of nesquehonite (50 °C) from locality Hodkovce 2.

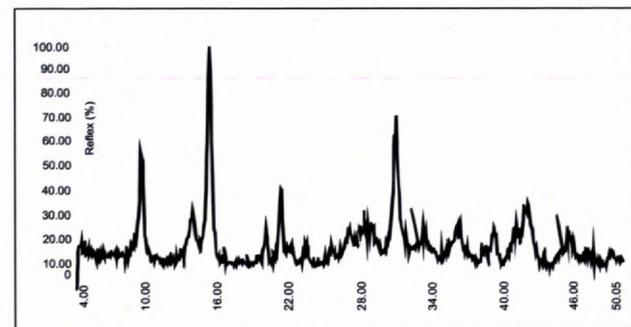
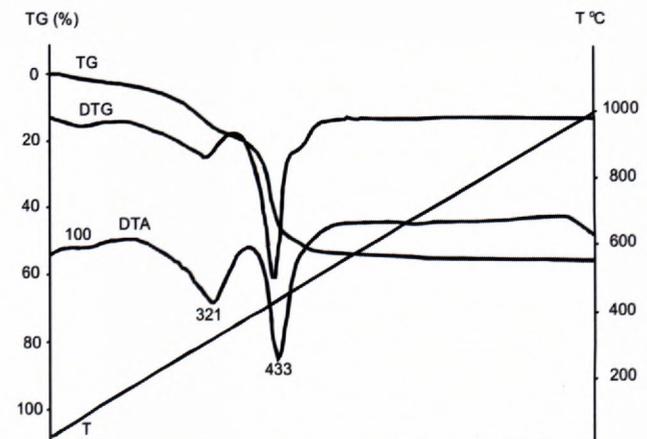


Fig. 4. X-ray diffraction record of hydromagnesite (200 °C) from locality Hodkovce 2.



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6. Literature

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