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## ON THE FORMATION OF RETGERSITE FROM CHELMIEC

UKD 549.766.01/.07:535.84:548.73:543.226:548.73  
(438.262 Chelmiec)

**Abstract.** The origin of retgersite from the vicinity of Chelmiec is discussed and its physical properties, X-ray and thermal data, and infra-red absorption spectrum are given. Author suggests that retgersite was formed by dehydration of morenosite, which was a primary weathering product of gersdorffite.

**Occurrence.** Retgersite,  $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$ , reported till now only from very few places (Fron del & Palache 1949, Eliseev & Smirnova 1958, Fedotova 1967) was recently described from Chelmiec, Góry Kaczawskie Mts., Lower Silesia (Paulo 1970). It was found among piled vein materials, the principal constituent of which is quartz with local concentrations of gersdorffite, galena, sphalerite, chalcopiryte, tetrahedrite, and other sulphides. Ore minerals usually form close intergrowths, e.g. in gersdorffite there occur fine inclusions and veinlets of piryte, marcasite, bismuthinite, sphalerite, chalcopiryte etc.

Gersdorffite is commonly covered with thin green efflorescences. They were subjected to more detailed investigations. Some weight was put upon the question of their origin and primary composition. It was found that these efflorescences were formed by hydrated nickel sulphates — morenosite or retgersite. Owing to instability of heptahydrate in laboratory conditions (Fron del & Palache 1949, Mellor 1961) it is difficult to establish the primary hydration stage of Ni-sulphate. Similar colour of both hydrates, especially in fine-grained crusts, makes additional difficulty in their distinction in field conditions.

The thickness of sulphate efflorescences on gersdorffite grew considerably when kept some years in laboratory store at temperature of about  $10^\circ\text{C}$  in rather humid conditions. The presence of predominant retgersite and admixture of morenosite in these efflorescences during subsequent study was established.

**Morphology and physical properties.** The majority of the grains forming the efflorescences does not exceed 0.2 mm in diameter. Well developed crystals are seldom. They have fibrous or tabular

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habit and positive elongation. Perpendicular to 001 octangles with tetragonal symmetry were found.

In tufts emerald green, in thin fragments pale green, almost colourless, perfectly transparent. Luster vitreous. Uniaxial negative,  $n_{\omega} = 1,487 \pm 0.001$ ,  $n_e = 1,511 \pm 0.002$  (measured by immersion method in Na-light). Brittle. Perfect cleavage along 001.

X-ray characteristics. X-ray analyses were carried out by the powder method using 114.8 diameter cameras and monochromatic  $\text{CoK}_{\alpha}$  radiation. To obtain powder specimens the materials under study were ground directly in acetylcellulose glue to prevent their dehydration. The identity of investigated substance and that of artificial  $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$  crystals was confirmed (Table 1). Lattice parameters, calculated from 200, 400, 004 and 00.12 lines are:  $a_0 = 6.82 \text{ \AA}$ ;  $c_0 = 18.46 \text{ \AA}$ ;  $a_0 : c_0 = 1 : 2.71$ .

On powder patterns of microcrystalline material from inner part of efflorescence weak lines 5.95; 5.49; 5.10; 4.93; 3.61  $\text{\AA}$  (broad) etc. and moderately strong ones 4.41; 4.04; 2.886  $\text{\AA}$ , characteristic of morenosite (Fig. 1), were also present.

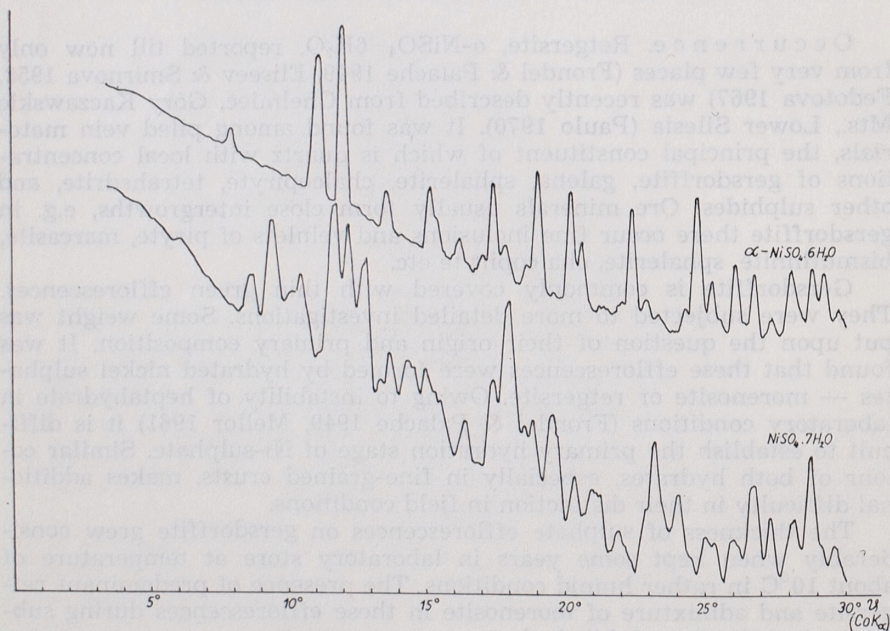


Fig. 1. A comparison of microphotometer tracings of X-ray films of nickel sulphate hydrates

The powder data obtained (Table 1) are more complete than those of Hanawalt et al. (1938) often used as standard ones. They differ slightly from those of Eliseev & Smirnowa (1958) and Fedotova (1967), evidently

Table 1

A comparison of  $\alpha\text{-NiSO}_4 \cdot 6\text{H}_2\text{O}$  X-ray powder patterns  $\text{CoK}_{\alpha}$

No.	hkl	Artificial crystals		Retgersite from Chelmiec	
		I	d (Å)	I	d (Å)
1	101	2	6.45	3	6.47
2	111, 103, 004	8	4.61	8	4.61
3		1	4.43	1	4.43
4	112	10	4.27	10	4.28
5		0,5	4.12	0,5	4.11
6			—	0,5	4.04
7	104	3	3.779	2	3.784
8	200	4	3.399	3	3.405
9	105	2	3.343	1	3.349
10	202	2	3.186	2	3.201
11		1	3.032	0,5	3.041
12	203	6	2.964	5	2.975
13		3	2.897	2	2.909
14		1	2.782	1	2.783
15	204	8	2.725	6	2.733
16	116	7	2.572	5	2.580
17		4	2.525	3	2.536
18		0,5	2.372		—
19	215	7	2.334	5	2.336
20		1	2.289		—
21		0,5	2.247	0,5	2.249
22		1	2.158	0,5	2.167
23	224, 310	8	2.124	5	2.132
24	118	3	2.087	2	2.093
25		1	2.050		—
26	313	4	2.023	3	2.027
27	217	4	1.9764	2	1.9818
28		1	1.9379		—
29			—	0,5	1.9503
30	226	4 d	1.8899	3	1.8954
31	315	3	1.8451	2	1.8510
32	218	3	1.8206	1	1.8273
33		1	1.7918	0,5	1.7984
34	209, 316	4	1.7522	3	1.7543
35	400	4	1.7054	3	1.7083
36		3	1.6854	1	1.6868
37	228	4	1.6515	2	1.6528
38		2	1.6317	1	1.6338
39	404	3	1.5892	1	1.5896
40		1 d	1.5672		—
41	00.12	1 d	1.5354	0,5 d	1.5395
42	420	3	1.5196	2 d	1.5203
43		2	1.5098	1	1.5120



Table 1 (continued)

No.	hkl	Artificial crystals		Retgersite from Chelmiec	
		I	d (Å)	I	d (Å)
44		1	1.4932	—	—
45		2	1.4710	1	1.4727
46		1	1.4369	0.5	1.4379
47		1	1.4190	0.5	1.4193
48		1	1.3954	1	1.3984
49		2	1.3873	2	1.3882
50		1	1.3777	—	—
51		1 d	1.3562	1 d	1.3589
52		1	1.3239	—	—
53		2	1.3090	1	1.3098
54		2	1.2968	1	1.2977
55		1 d	1.2832	0.5	1.2823
56		4	1.2571	2	1.2578
57		1	1.2475	—	—
58		1 d	1.2129	1 d	1.2121
59		1	1.1996	—	—
60		2 d	1.1837	1 d	1.1857
61		1 d	1.1651	—	—
62		2 d	1.1592	0.5	1.1612
63		2 d	1.1401	—	—
64		1 d	1.1255	—	—
65		2 d	1.1118	1 d	1.1126
66		1 d	1.0806	—	—
67		2 d	1.0357	1 d	1.0365
68		2 d	1.0299	—	—
69			1.0106	—	—
70		1	1.0082	—	—
71			0.9922	—	—
72		2	0.9872	—	—
73		1 d	0.9479	—	—
74		1	0.9384	—	—
75		0.5	0.9355	—	—
76		2 d	0.9245	—	—
77		2 d	0.9178	—	—
78		1 d	0.9140	—	—
79		1 d	0.9110	—	—
80		2 d	0.8992	—	—

Indices after Hanawalt et al. (1938), d — diffused line

partly due to relatively high admixture of morenosite in retgersite samples examined by both authors.

**Chemical properties and composition.** Easily soluble in water. Contains (semiquantitative spectral analysis): Ni — main, As —

1—5%, Fe, Bi — in the order of 0.1%, Co, Sb — in the order of 0.01%, traces of Mg, Zn, Pb, Cu, Mn. The presence of arsenic in examined sample is probably due to gersdorffite and/or some arsenate impurities.

**Thermal characteristics.** Differential thermal analyses were performed in noncommercial apparatus with six-cavity cylindrical ceramic (alundum) sample holder, in which three cavities were filled with 0.03 g of investigated substance each, at the heating rate of 12°C/min. DTA curve obtained (Fig. 2) was compared with those of arti-

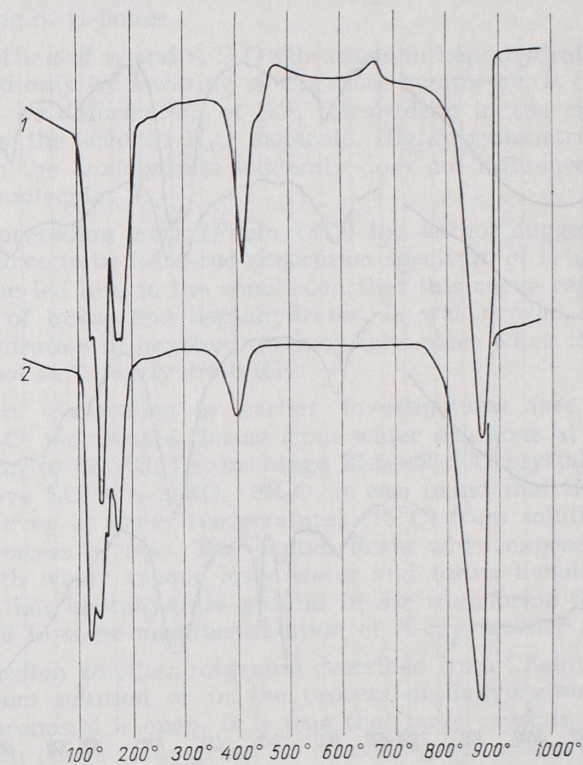


Fig. 2. DTA curves of hydrated nickel sulphates  
1 — retgersite from Chelmiec, 2 —  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  artificial

ficial  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ . The curves of the both hydrates show similar endothermic effects at about 140, 175, and 400°C, connected with polystadial dehydration, and a strong effect at 860°C due to decomposition of  $\text{NiSO}_4$  to NiO. The thermogram of heptahydrate shows an additional strong effect at 120°C connected with the expulsion of the seventh  $\text{H}_2\text{O}$  molecule. These results agree in general with those of Berg et al. (1954) and Kubas & Szalkowicz (1968) obtained for artificial  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ . The peaks at 180, 400(?), 470, and 670°C on the curve of



studied substance are probably due to impurities in natural material. Weak effect at 120°C may be evoked by morenosite admixture. At this temperature, however, also polymorphic transformation of  $\alpha$ -NiSO<sub>4</sub> · 6H<sub>2</sub>O to  $\gamma$ -NiSO<sub>4</sub> · 6H<sub>2</sub>O occurs (Hideaki Chihara et al. 1953).

**Infra-red characteristics.** The absorption curves (Fig. 3) were obtained on UR-10 (Zeiss) spectrophotometer using KBr discs and Nujol mull techniques. On the absorption curve of artificial heptahydrate the most intensive absorption band between 1000 and 1300 cm<sup>-1</sup>,

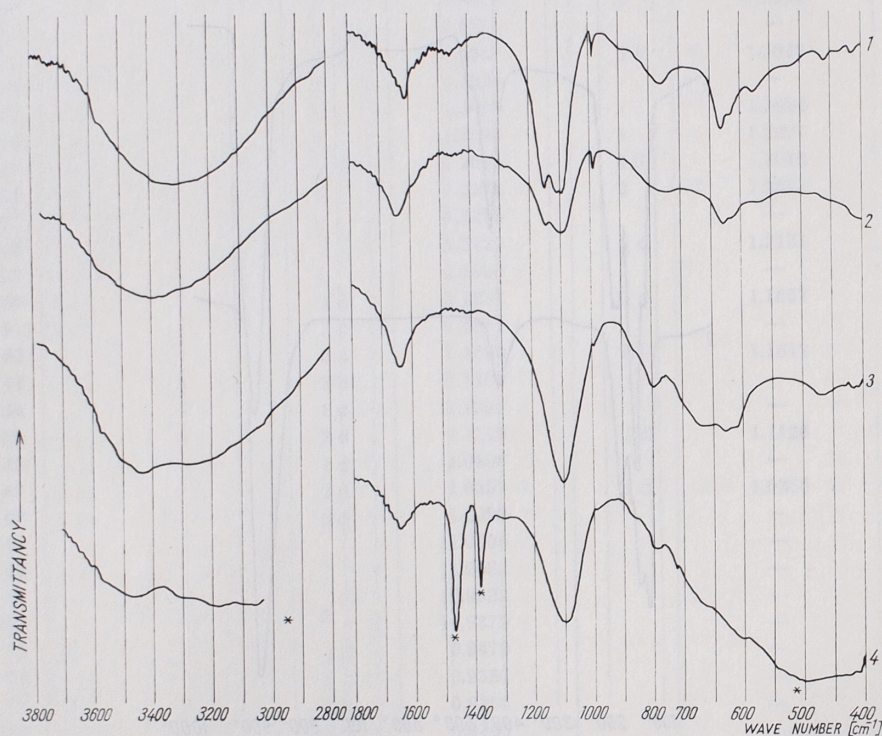


Fig. 3. Infra-red absorption spectra of nickel sulphate hydrates  
1 — NiSO<sub>4</sub> · 7H<sub>2</sub>O (artif.), 2 — retgersite-morenosite from Chelmiec, 3 — retgersite from Chelmiec, 4 — NiSO<sub>4</sub> · 6H<sub>2</sub>O (artif.). Curves 1 — 3 obtained by KBr pellet technique, curve 4 by Nujol mull technique. Asterisks (\*) denote Nujol bands

connected with  $\nu_3$  vibrations of sulphate ion, is clearly split into three components: 1094, 1107, and 1147 cm<sup>-1</sup>. This indicates complete removal of degeneracy. Sharp maximum at 988 cm<sup>-1</sup> was ascribed to activated  $\nu_1$  vibration. The  $\nu_4$  band of SO<sub>4</sub> shows, like  $\nu_3$ , a splitting into its components 578, 617, and 632 cm<sup>-1</sup>. Water molecules bending vibrations between 1550 and 1750 cm<sup>-1</sup> have a maximum frequency at 1618 cm<sup>-1</sup> with

additional weak band at 1470 cm<sup>-1</sup>. O-H stretching vibrations of H<sub>2</sub>O are represented by an extensive band at 2800—3700 cm<sup>-1</sup>. The distinct band at 760 cm<sup>-1</sup> corresponds most probably to H<sub>2</sub>O librations. It may be that the remaining bands at 416 and 432 cm<sup>-1</sup> are due to H<sub>2</sub>O wagging frequencies.

On the contrary the hexahydrate curve shows in the  $\nu_3$  and  $\nu_1$  regions only single absorption bands corresponding to degenerate S-O vibrations. The H-O-H bending as well as the O-H stretching vibrations shift to higher wave numbers. The latter phenomenon should be ascribed to weakening of H-bonds.

The splitting of  $\nu_3$  and  $\nu_4$  S-O vibrations in heptahydrate is too strong to be caused only by lowering of the space symmetry. It could be partly evoked by the deformation of SO<sub>4</sub> tetrahedron in the crystalline field distorted by the seventh H<sub>2</sub>O molecule. Highly symmetrical {Ni(H<sub>2</sub>O)<sub>6</sub>} grouping in the hexahydrate evidently does not influence the structure of the SO<sub>4</sub> molecule.

In the preceding work (Paulo 1970) the author suggested the No. 2 on Fig. 3 curve to be infra-red absorption spectrum of retgersite. Present investigation led him to the conclusion that this curve represents rather a mixture of hexa- and heptahydrates. It was proved experimentally that the hydration of hexahydrate may take place when the disc is pressed, from not sufficiently dried KBr.

**Origin.** According to earlier investigations (see Mellor 1961) NiSO<sub>4</sub> · 7H<sub>2</sub>O, morenosite, forms from water solutions at ordinary temperatures up to 31.5°C. In the range 31.5—53.5°C crystallizes  $\alpha$ -NiSO<sub>4</sub> · 6H<sub>2</sub>O, above 53.5°C  $\gamma$ -NiSO<sub>4</sub> · 6H<sub>2</sub>O. It was found that the hexahydrate may form even at lower temperatures (15°C) from solutions containing sufficient excess of acid. The heptahydrate when exposed to air unsaturated with water vapour loses water and forms hexahydrate. It was found too that heptahydrate ground in air transforms to hexahydrate. It may lead to some misinterpretation of X-ray powder patterns.

The question whether retgersite described from Chelmiec crystallized directly from solution or in the process of dehydration of originally formed morenosite is open. It is true that large crystals of both hydrates differ in shade (blue-green or emerald-green respectively), the colour however of fine grained materials is similar and therefore makes difficult their distinction. It is to be expected that at laboratory and certain field conditions the more stable phase — retgersite should be found. Paragenetic association of retgersite and morenosite as well as a higher content of the latter in the inner part of the efflorescence may lead to the conclusion that retgersite described was formed from morenosite.

**Acknowledgements.** I am greatly indebted to J. Kubisz for numerous helpful suggestions and his criticism of an early version of the manuscript. My thanks are also due to J. Fijał for infra-red absorption curves and assistance in their interpretation, to M. Hubicka-Ptasińska for spectral determinations, to K. Feliś for DTA curves, and to B. Wiecheć for preparing X-ray patterns.



- [BERG et al.] 1954: БЕРГ Л. Г., НИКОЛАЕВ А. В., РОДЭ Е. И. — Термография. Москва — Ленинград.
- [ELISEEV & SMIRNOVA], 1958: ЕЛИСЕЕВ Э. Н., СМІРНОВА С. И. — Железисто-магнитный ретгерсит. — Зап. Всесоюз. Минер. Общ., 87, 1.
- [FEDOTOVA], 1967: ФЕДОТОВА М. Г. — Ретгерсит Аллареченского месторождения. — Материалы по минералогии Кольского полуострова, 5, 70—73. Ленинград.
- FRONDEL C., PALACHE C., 1949: Retgersite,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ , a new mineral. — Amer. Miner., 34, 188—194.
- HANAWALT J. D., RINN N. W., FREVEL L. K., 1938: Chemical analysis by X-ray diffraction. — Ind. and Eng. Chem., Anal. Ed., 10, 457—512.
- HIDEAKI CHIHARA, SHUZO SEKI, 1953: Bull. Chem. Soc. Japan., 26, 88—92 (cit. after Kubas et al., 1968).
- KUBAS Z., SZALKOWICZ M., 1968: Badania derywatograficzne dehydratacji siedmiowodnego siarczynu niklawego. — Zesz. nauk. AGH. 215, 1—10 Kraków.
- MELLOR J. W., 1961: A comprehensive treatise on inorganic and theoretical chemistry, 15. London.
- PAULO A., 1970: Minerale niki i bizmutu w żyłach kruszcowych okolicy Chelmcza (Góry Kaczawskie, Dolny Śląsk). — Pr. Miner. Kom. Nauk. Miner. PAN Oddz. w Krakowie 24, 61—82.

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## ZAGADNIENIE GENEZY RETGERSYTU Z CHELMCA

### Streszczenie

Opisano środowisko występowania retgersytu w rejonie Chelmcza (Dolny Śląsk), a także podano charakterystykę tego rzadkiego minerału metodami optycznymi, rentgenowskimi, termicznymi i spektrofotometrycznymi w podczerwieni. Autor sugeruje, że retgersyt powstał w cyklu wietrzeniowym: gersdorffit (hypogeniczny) → morenosyt → retgersyt. Dehydratacja morenosytu mogła nastąpić zarówno w warunkach naturalnych, jak i laboratoryjnych.

### OBJASNIENIA FIGUR

- Fig. 1. Zestawienie mikrofotogramów filmów rentgenowskich uwodnionych siarczanów niklu
- Fig. 2. Krzywe DTA uwodnionych siarczanów niklu  
1 — retgersyt z Chelmcza, 2 — syntetyczny  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
- Fig. 3. Widma absorpcyjne w podczerwieni uwodnionych siarczanów niklu  
1 —  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  (syntetyczny), 2 — retgersyt-morenosyt z Chelmcza, 3 — retgersyt z Chelmcza, 4 —  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (syntetyczny). Krzywe 1 — 3 otrzymano techniką pastylek z KBr, krzywą 4 — techniką zawieszinową w oleju parafinowym. Gwiazdki \* oznaczają pasma absorpcyjne oleju

## ПРОБЛЕМА ГЕНЕЗИСА РЕТГЕРСИТА ИЗ ХЕЛМЦА

### Резюме

В статье описаны условия распространения ретгерсита в районе Хелмца (Нижняя Силезия) и дана характеристика этого редкого минерала, основанная на анализах оптическим, рентгеновским, термическим и инфракрасным спектральными методами. Автор предполагает, что ретгерсит образовался в процессе выветривания: герсдорffit (гипогенный) → моренозит → ретгерсит. Дегидратация моренозита могла произойти как в естественных, так и лабораторных условиях.

### ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Сопоставление микрофотограмм из дебаграммов гидросульфатов никеля

Фиг. 2. Кривые ДТА гидросульфатов никеля

1 — ретгерсит из Хелмца, 2 — синтетический  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$

Фиг. 3. Инфракрасные спектры поглощения гидросульфатов никеля

1 —  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  (синтетический), 2 — ретгерсит-моренозит из Хелмца, 3 — ретгерсит из Хелмца, 4 —  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (синтетический). Кривые 1—3 получены методом прессованных таблеток с KBr, кривая 4 способом суспензии в парафиновом масле. Звездочки \* обозначают спектры поглощения масла