Geoderma 163 (2011) 95–108

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Technogenic soils developed on mine spoils containing iron sulphides: Mineral transformations as an indicator of pedogenesis

Łukasz Uzarowicz [a,*], Stefan Skiba [b]

[a] Faculty of Geodesy and Cartography, Warsaw University of Technology, Pl. Politechniki 1, 00-661 Warsaw, Poland
[b] Institute of Geography and Spatial Management, Jagiellonian University, ul. Gronostajowa 7, 30-387 Krakow, Poland

ARTICLE INFO

Article history:
Received 25 June 2010
Received in revised form 2 April 2011
Accepted 7 April 2011

Keywords:
Technosols
Sulphide weathering
Sulphates
Iron oxides
Swelling clay minerals
Soil classification

ABSTRACT

Technogenic soils (*Technosols*) containing iron sulphides, developed on mine spoils located in three abandoned industrial sites in Poland (the “Siersza” hard coal mine in Trzebinia, “Staszic” pyrite mine in Rudki, and pyrite mines in Wieściszowice), were investigated in order to identify the most important mineral transformations occurring in the soils. The X-ray diffraction (XRD), scanning electron microscope-energy dispersive spectrometry (SEM-EDS) techniques, and selective extraction methods were applied in the examination of soil mineralogy. The soils studied represented weakly developed soil formations in which organic matter accumulation increasing with age was observed, along with intense weathering of parent materials containing iron sulphides. The degree of sulphide transformations is age-dependent. In young soils from Trzebinia and Rudki, poorly weathered iron sulphides occurred, whereas in old soils from Wieściszowice, iron sulphides were almost entirely transformed. The main products of sulphide weathering are iron oxides and sulphate minerals (gypsum and jarosite group minerals mainly). Inherited phyllosilicates and pedogenic clay minerals (smectite, vermiculite, kaolinite, and mixed-layer minerals) were present in the soils studied. The development of Al-hydroxy interlayers and the possibility of the formation of poorly crystalline Al phases were also documented. The processes seem to be pH-dependent and occur at pH ranging from 4.3 to 4.4. The development of iron oxides and sulphate minerals in the process of sulphide weathering, as well as phyllosilicate transformations (e.g. the development of swelling clay minerals at the expense of inherited mica and chlorite, and the formation of hydroxy interlayers in clay minerals) are the main mineralogical aspects of pedogenesis of technogenic soils developed on mine spoils containing iron sulphides. The WRB and Soil Taxonomy systems require more precise solutions concerning the classification of technogenic soils investigated. The *thionic* horizon (WRB) and *sulfuric* horizon (Soil Taxonomy) definitions, as well as the *sulphidic material* (WRB) and *sulfidic material* (Soil Taxonomy) definitions need to be supplemented. The paper suggests the introduction of the *Sulfic Udorthents* taxon in the Soil Taxonomy, as well as the introduction of “Thionic” suffix qualifier to the key to the *Technosols* in the WRB.

1. Introduction

Sulphide minerals rarely occur in soils because of their instability in weathering environments. Natural accumulation of sulphides and products of their decay was documented in acid sulphate soils occurring in coastal regions all over the world (Doner and Lynn, 1989; Fanning et al., 2002; Pracz and Kwasowski, 2001; Ritsema et al., 2000). The main mineral developing in such soils is pyrite the precursors of which are iron monosulphides (e.g. Smith and Melville, 2004). Excluding coastal regions, sulphide minerals are a very rare component of natural soils. They occur in peat soils, periodically flooded soils (Siuta and Rejman-Czajkowska, 1980), as well as soils developed on outcrops of sulphide-bearing rocks.

The presence of sulphide minerals in soils is often caused by anthropogenic factors. As a result of mining activity, sulphide-bearing wastes are deposited on the earth's surface (e.g. Johnson, 2003; Krzaklewski, 1990; Strzyszcz, 1978, 1989; Twardowska et al., 1988). Soils containing sulphides occur, for instance, on mine spoils of sulphide mines and mine spoils of hard and brown coal mines, where dispersed iron sulphide mineralization in coal seams is present.

In the weathering environment, sulphides react with oxygen and water with a participation of microorganisms. As a result, metals are released, and sulphuric acid $(2H^+ + SO_4^{2-})$ is produced, causing strong acidity (Bolan et al., 2005). Investigations by Jennings et al. (2000) proved that high acidity is caused by oxidation of sulphides such as pyrite, arsenopyrite, chalcopyrite, pyrrhotite, marcasite, and sphalerite. Oxidation of certain sulphide minerals (e.g. galena and chalcocite) does not increase acidity.

Soils developed on mine spoils containing iron sulphides, despite their anthropogenic origin, undergo natural processes such as

---

* Corresponding author. Fax: +48 22 234 71 42.
E-mail address: luzarowicz@gik.pw.edu.pl (Ł Uzarowicz).

0016-7061/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.geoderma.2011.04.008

weathering and soil-forming processes (e.g. Barnhisel and Massey, 1969; Bzowski and Strzyszcz, 1993; Kostenko and Opanasenko, 2005; Skawina, 1959a,b; Struthers, 1964). One of the most important aspects of natural functioning of initial soils developed on mine spoils are mineral transformations of industrial wastes. To the best of the author's knowledge, such transformations in technogenic soils developed on sulphide-bearing mine spoils have not yet been studied in detail (e.g. Barnhisel and Massey, 1969; Uzarowicz et al., 2008). Mineral transformations in weathering environments, similar to those encountered in technogenic soils containing iron sulphides (e.g. in soils under the influence of acid mine drainage, in acid sulphate soils, or in overburdens of brown coal mines) have been investigated to a larger extent (e.g. Dixon et al., 1982; Dubiková et al., 2002; Martín et al., 2008; Ross et al., 1988; Šucha et al., 2002). Such investigations led to the conclusion that sulphide weathering results in the development of iron oxides and many sulphate minerals. Similar transformations occur in sulphide weathering zones (Bigham et al., 1996; Lintnerová et al., 1999; Murad and Rojík, 2003; Parafiniuk, 1991, 1996; Parafiniuk and Siuda, 2006; Singh et al., 1999; Wieser, 1949). In acid soils and mine wastes containing iron sulphides, intense phyllosilicate transformations occur (e.g. Barnhisel and Rotromel, 1974; Bzowski and Strzyszcz, 1993; Dixon et al., 1982; Uzarowicz et al., 2008). These transformations lead to the development of swelling clay minerals and dissolution of less resistant clay minerals. Such transformations were also documented in sulphide-bearing rock weathering zones (e.g. De Kimpe and Miles, 1992), as well as in soils and deposits influenced by acid mine drainage (e.g. Dubiková et al., 2002; Galan et al., 1999; Šucha et al., 2002).

The objective of this paper was to investigate in details sulphide and phyllosilicate transformations, which are one of the most important mineralogical aspects of pedogenesis of technogenic soils developed on mine spoils containing iron sulphides. The data obtained were the base for a discussion on the classification of the soils studied.

2. Materials and methods

2.1. Study area and materials studied

Soil profiles developed on mine wastes (mine spoils, post-flotation sludges) were investigated (Table 1). The study areas were located in three abandoned industrial sites in Poland: (1) abandoned hard coal mine “Siersza” in Trzebinia town (Silesian Uplands), closed in 1999, (2) abandoned pyrite mine “Staszic” in Rudki village (Holy Cross Mts.), closed in 1971, and (3) abandoned pyrite mines in Wieściszowice village (Rudawy Janowickie Mts. Western Sudetes Mts.), closed in 1925.

Mine wastes investigated varied in age. The “Siersza” hard coal mine ceased mining exploitation in 1999, thus the soils developed on the surface of the dump are several years old. They had not been reclaimed before the investigation was completed. Land in the area of the “Staszic” pyrite mine was reclaimed in the 1970s, thus the soils developed there are approximately 40 years old. Mining exploitation in the Wieściszowice region continued between 1785 and 1925, thus the soils on the dumps may be 100–200 years old. They have not been reclaimed.

2.2. Analytical methods

Soil properties (Table 2) were analysed using common pedological methods (van Reeuwijk, 2002). Soil colour (dry and wet) was determined using Munsell Soil Colour Charts. Texture was determined using the Casagrande method (for < 1 mm fraction) and by dry-sieving (for 2 and 1 mm fraction). The content of rock fragments was determined by dry-sieving. The pH (in distilled water and 1 M KCl) was analysed potentiometrically based on air-dry samples of fine earth using a soil/solution ratio of 1:2.5 (for organic samples the ratio was 1:10). The concentration of organic carbon was determined using dichromate oxidation techniques (modified Tyurin method; digestion reagent: $K_2Cr_2O_7$ and H_2SO_4; titrant: $FeSO_4 \cdot 7H_2O$). The content of carbonates was determined using the Scheibler volumetric method (reagent: 10% w/w HCl). Soil units were determined according to the World Reference Base for Soil Resources (IUSS, 2006) and Soil Taxonomy (Soil Survey Staff, 1999).

Clay fractions were separated from bulk soil samples (<2 mm) according to the Jackson's procedure (Jackson, 1975) including carbonate removal using acetic acid buffer (pH ~5), organic matter removal using 30% hydrogen peroxide buffered with an acetic acid buffer with the pH of ~5 (during the organic matter removal the pH of the solution was strictly controlled to avoid an abrupt decrease of pH in the process of sulphide oxidation by peroxide which may potentially alter

Table 1
Location and description of the soils investigated.

Profile	Geographical position	Field setting	Vegetation	Soil description
T1	Trzebinia Lat. 50°11′32.5″ N Long. 19°26′32.9″ E Alt. 338 m a.s.l.	Surface of a dump	None	Very weakly developed soil profile containing large amounts of crashed hard coal in the topsoil (C1 horizon) and grey loamy material in the subsoil (C2 horizon).
T2	Trzebinia Lat. 50°11′38.1″ N Long. 19°26′30.2″ E Alt. 341 m a.s.l.	Northern slope of the dump	None	Very weakly developed soil profile. The black layers (C1 and C3 horizons) contained large amounts of crashed hard coal. C2 horizon consisted of grey loamy material, and C4 horizon consisted of orange and rusty sandy loam.
R1	Rudki Lat. 50°53′49.0″ N Long. 21°05′58.3″ E Alt. 224 m a.s.l.	Former flotation tank	Meadow	Very weakly developed and bipartite soil profile. In the subsoil (C2 horizon), brown post-flotation sludge containing carbonates and iron sulphides occurred. The topsoil (A and C1 horizons) consisted of brown and orange loamy material deposited on flotation tanks during reclamation.
R2	Rudki Lat. 50°53′35.8″ N Long. 21°04′49.8″ E Alt. 253 m a.s.l.	Even, not neutralized surface of the former mine waste dump “Serwis”	Meadow	Very weakly developed soil profile developed on the border of an extremely acid area with no plant cover. The entire profile was brown and rusty, and the separated horizons (from C1 to C4) slightly differed in color. In C4 horizon, several centimeter large rock fragments composed of iron sulphides were found.
W1	Wieściszowice Lat. 50°49′43.6″ N Long. 15°58′23.2″ E Alt. 555 m a.s.l.	Surface of a stony dump	Spruce and beech forest	Weakly developed stony soil profile. In the topsoil (A1 and A2 horizons), relatively large amounts of soil organic matter characterized by various stages of decomposition were accumulated. In C horizon, rusty and brown spots, not forming a continuous horizon, were visible.
W2	Wieściszowice Lat. 50°49′50.1″ N Long. 15°58' 21.4″ E Alt. 550 m a.s.l.	Surface of a fine earth dump	Sparse birch and pine forest	Weakly developed soil profile characterized by alternating sandy and silty-loam technogenic layers. White and grey spots as well as rusty trails resulting from oxydo-reduction (gleyic) processes and migration of iron occurred in the whole profile.

Table 2
Properties of the soils investigated.

Profile	Depth (cm)	Horizon	Soil colour		Percentage of fraction (in mm)			Content of rock fragments (%)	pH		Content of organic carbon (%)	Content of carbonates (%)
			Moist	Dry	2.0–0.05	0.05–0.002	<0.002		H_2O	KCl		
T1	0–10	C1	N 1.5/0	N 3/0	80	15	5	18	2.5	2.3	–	n
	10–35	C2	N 2/0	N 4/0	44	37	19	44	2.5	2.4	10.4	n
T2	0–40	C1	N 1.5/0	N 3/0	–	–	–	–	2.4	2.4	–	n
	40–76	C2	10 YR 3/1	10 YR 5/1	50	35	15	33	3.4	3.3	7.4	n
	76–98	C3	10 YR 2/1	10 YR 4/1	44	36	20	23	3.1	3.0	14.8	n
	98–105	C4	10 YR 4/4	2.5 Y 6/4	76	14	10	30	2.4	2.3	1.6	n
R1	0–1	Oi	–	–	–	–	–	–	–	–	–	–
	1–3	A	7.5 YR 3/3	7.5 YR 5/3	45	33	22	20	7.3	6.9	5.2	3.0
	3–30	C1	7.5 YR 5/4	10 YR 6/6	40	20	40	28	7.2	6.7	0.9	2.4
	30–95	C2	7.5 YR 3/3	7.5 YR 5/4	59	37	4	0	7.4	7.4	–	60.3
R2	0–2	Oi	–	–	–	–	–	–	–	–	–	n
	2–7	A	10 YR 4/2	10 YR 5/4	69	17	14	2	4.4	4.0	2.5	n
	7–14	C1	10 YR 4/4	10 YR 7/4	47	29	24	12	4.3	4.1	0.6	n
	14–30	C2	10 YR 3/4	10 YR 6/4	51	29	20	22	3.0	2.8	0.3	n
	30–60	C3	10 YR 4/4	10 YR 6/3	52	26	22	24	2.7	2.4	0.3	n
	60–75	C4	10 YR 4/3	10 YR 6/3	54	28	18	20	3.3	3.1	–	n
W1	0–1	Oi	–	–	–	–	–	–	4.8	4.3	–	n
	1–4	Oe	–	–	–	–	–	–	4.0	3.4	–	n
	4–9	A1	10 YR 2/2	10 YR 4/2	74	15	11	57	3.9	3.3	9.9	n
	9–10	A2	10 YR 2/3	10 YR 5/3	71	19	10	51	4.0	3.4	4.9	n
	10–45	C	10 YR 6/6	10 YR 7/6	75	17	8	70	3.9	3.5	0.7	n
W2	0–1	Oi	–	–	–	–	–	–	–	–	–	n
	1–4	A	10 YR 4/2	10 YR 6/3	75	18	7	3	4.2	3.5	2.6	n
	4–15	AC	10 YR 5/6	10 YR 7/6	65	28	7	0	4.2	3.6	1.0	n
	15–30	C1	2.5 Y 6/8	2.5 Y 8/6	11	68	21	0	4.3	3.6	0.5	n
	30–35	C2	10 YR 5/6	10 YR 7/8	86	9	5	1	4.4	3.9	0.9	n
	35–86 rusty	C3	2.5 Y 6/6	2.5 Y 8/6								
	35–86 white	C3	2.5 Y 7/2	2.5 Y 8/1	11	70	19	0	4.3	3.6	0.5	n
	86–112	C4	2.5 Y 6/6	2.5 Y 7/6	87	8	5	0	4.3	4.1	0.9	n

– Not determined.
n—Lack of carbonates.

the layer silicates), and free oxides removal according to the Mehra and Jackson (1960) method using sodium dithionite buffered with citrate–bicarbonate solution. Soil samples were centrifuged after the Jackson's procedure in order to separate clay fractions (<2 μm and<0.2 μm), which were subsequently Na-, Mg- and K-saturated and dialyzed. Oriented mounts on the glass slides were prepared from clay fractions by sedimentation. The X-ray diffraction (XRD) analyses were performed on the mounts in air-dry conditions (Mg-saturated and K-saturated samples), after glycerol saturation (Mg-saturated samples only), and after heating at 330 °C and 550 °C sequentially (K-saturated samples only). In certain cases (<0.2 μm clay fraction from Wieściszowice soils), XRD analyses for all diagnostic tests (ethylene-glycol saturation, heating) were performed on Na-saturated clays.

XRD analyses of bulk soil samples (<2 mm) and clay fractions were performed with the use of a Philips X'Pert diffractometer with the generator PW1870 and the vertical goniometer PW3020, equipped with a 1° divergence slit, 0.2 mm receiving slit, incident- and diffracted-beam Soller slits, 1° anti scatter slit, and a graphite diffracted-beam monochromator. CuKα radiation was used with the applied voltage of 40 kV and 30 mA current. Random mounts of bulk soil material and oriented mounts of clay fraction were scanned from 2 to 64°2Θ at a counting time of 1 s per 0.02° step.

The selected 1–2 mm fractions of soils were impregnated by Araldite 2020 epoxy resin in order to determine the degree of iron sulphide weathering. Polished thin sections were prepared from the impregnated soil materials. They were examined in both transmitted and reflected light with the use of an optical microscope, as well as scanning electron microscope (SEM). Polished thin sections were prepared in the Department of Soil Science and Soil Geography, Institute of Geography and Spatial Management, Jagiellonian University, Krakow, Poland.

The selected air-dried soil samples and thin sections from the soil material were studied using a SEM. A field emission scanning electron microscope (Hitachi S-4700) equipped with a Vantage Noran EDS microanalysis system and a back-scattered electrons detector (YAG BSE), was used. Natural surfaces of the soil samples and the polished thin sections were carbon-coated and examined by SEM. The clay mineral separation, XRD analyses, and SEM studies were performed in the Institute of Geological Sciences, Jagiellonian University, Krakow, Poland.

Air dried <2 mm soil samples were submitted to selective extractions in order to determine the forms of Fe, Al, and Si in the soils. Procedures compiled by Loeppert and Inskeep (1996) were applied. Three extractions were performed with the use of:

- dithionite–citrate–bicarbonate (extraction of Fe_{dith}),
- 0.175 M (pH 3.0) ammonium oxalate in the dark (extraction of Fe_{ox}, Al_{ox}, and Si_{ox}),
- 0.1 M (pH 10.0) Na–pyrophosphate (extraction of Fe_{pyr} and Al_{pyr}).

The concentrations of elements in soil extracts were measured using the ICP-AES method with the use of a Plasma 40 (Perkin Elmer) apparatus. The analyses were carried out in the Hydrogeochemical Laboratory of the Faculty of Geology, Geophysics and Environment Protection, AGH University of Science and Technology, Krakow, Poland.

2.3. XRD patterns interpretation

XRD patterns of bulk soil samples and oriented mounts of soil clay fractions were interpreted according to guidelines specified by Brindley and Brown (1980), Moore and Reynolds (1997), and Środoń (2006). The detailed interpretation of chlorite, vermiculite, and hydroxy-interlayered swelling minerals was carried out with the use of criteria specified by Barnhisel and Bertsch (1989), and Lagaly et al. (2006). The XRD patterns were processed using the ClayLab computer program (Mystkowski, 1999).

3. Results and discussion

3.1. Soil properties and pedogenesis

The investigated soils represented weakly developed technogenic soils. The soil material consisted mainly of post-mining wastes occurring as noticeable layers (C1, C2, etc.) in the soil profiles (Table 2). The development of O and A horizons occurring in the topsoil of soils investigated depended on the age of soil and the type of vegetation. The O and A horizons did not occur in very young soils from Trzebinia (T1 and T2 profiles) because of the lack of plant cover. Black layers in these soils contained crumbled hard coal deposited on the dump. In the topsoils of the Rudki (R1 and R2 profiles) and Wieściszowice (W1 and W2 profiles) soils, O and A horizons occurred, which maximum thicknesses ranged from 7 cm in Rudki to 10–15 cm in Wieściszowice. The best developed O and A horizons were present in W1 profile situated on the surface of an old dump covered by a spruce and beech forest (Tables 1 and 2). The W1 profile seems to be the best developed and probably the oldest soil investigated.

Accumulation of soil organic matter seems to be the only soil-forming process influencing the development of the investigated technogenic soils. The degree of the development of horizons containing soil organic matter is an important aspect of the functioning of technogenic soils, which may be an indirect indicator of the age of the soils. The progress of the soil organic matter accumulation in time is also one of the criteria of the estimation of the influence of the applied reclaiming methods on the development of technogenic soils (e.g. Šourková et al., 2005; Thomas and Jansen, 1985; Wójcik and Krzaklewski, 2007).

Apart from the accumulation of soil organic matter, no significant traces of other soil-forming processes were found in the soils investigated, by the research methods used. Various shades of brown (hue 10YR, values lower than 5 in moist conditions) and yellow (hue of 2.5Y, values higher than 7 in moist conditions) colours present in soils from Trzebinia and Wieściszowice (Table 2) occurred as spots and stains rather than continuous horizons. Therefore, their occurrence should be related to the intense weathering of sulphides or other iron-containing minerals rather than to the brownification process. Parts of the soil profiles where such colours occurred did not fulfil the requirements typical of *cambic* horizon according to the WRB classification system (IUSS, 2006). The absence of *cambic* horizons may constitute evidence of a low degree of the advancement of soil-forming processes in the technogenic soils studied. Various shades of brown colour (hue of 7.5YR, values lower than 5 in moist conditions) present in soils from Rudki (Table 2) resulted from the presence of iron oxides (goethite and hematite) inherited from parent rock.

In the W2 profile from Wieściszowice, greyish yellow (2.5Y 7/2) spots occurred (Table 2). The presence of such spots was most likely caused by oxydo-reduction (gleyic) processes. Any changes in the texture between horizons within soil profiles investigated were the effect of random deposition of post-mining wastes during technological processes rather than soil-forming processes. Such feature is typical of soils developing on mine spoils (e.g. Skawina, 1959b; Strzyszcz, 1978).

Most of the soils investigated were extremely acidic (pH_{H2O} from 2.4 to 4.4, Table 2) because of the presence of sulphuric acid—the result of acid sulphate weathering. Such a feature makes the soils investigated similar to acid sulphate soils representing the active

Table 3
Mineral composition of spoil materials and soils investigated.

Profile	Depth (cm)	Horizon	Primary minerals in spoil materials	Minerals in soils (determined by XRD and SEM)		
				Bulk (<2 mm) soil samples	Clay fraction < 2 µm	Clay fraction < 0.2 µm
T1	0–10	C1	Main minerals according to Twardowska et al. (1988) and Strzyszcz (1989): Q, Kf, K, M, Py, Ma, Fe oxides, Ch	**Q, K,** Kf, M, Gy, J, Ch?	**K, M,** Q, Ch, Kf, M/S? and/or M/V?	**K, M,** M/S? and/or M/V?, Q, Ch
	10–35	C2		**Q, Gy, Kf,** K, M, Ch, J	**K, M,** Ch, Q, M/S? and/or M/V?	**K, M,** M/S? and/or M/V?, Ch
T2	0–40	C1		**Q, K,** M, Gy, Kf, Ch?	**K, M,** Ch, Q, M/S? and/or M/V?	**K, M,** M/S? and/or M/V?
	40–76	C2		**Q, Gy, K,** M, Kf, Ch, J	**K, M,** Ch, Q, M/S? and/or M/V?	**K, M,** M/S? and/or M/V?, Ch
	76–98	C3		**Q, Kf,** Gy, K, M, Ch, J?	**K, M,** Ch, Q, M/S? and/or M/V?	**K, M,** M/S? and/or M/V?, Ch
	98–105	C4		**Q,** Kf, K, Gy, M, J, Ch?	**K, M,** Ch, Q, M/S? and/or M/V?	**K, M,** M/S? and/or M/V?, Ch
R1	0–1	Oi	Main minerals according to Skawina et al. (1974): Q, M, K, Ge, He, A, Kf, Py, Ma	–	–	–
	1–3	A		**Q,** Ge, Do, M, He, K, A, Gy?	**M, K,** Ge, Q, S?, Fs	**M, K,** Ge, Ch
	3–30	C1		**Q, Ge, Do,** K, M, He, A, Gy, Kf, Gi?	**K, M,** Ge, Q, Fs	**M, K,** Ge, S?
	30–95	C2	Main minerals according to Skawina et al. (1974): Do, Fe-sulfides (Py, Ma), Q, M	**Do, Gy,** Q, Ma, Py, Si	**M,** K, Ch, Q, Gi, A?, Fs	**M,** K
R2	0–2	Oi	Main minerals according to Skawina et al. (1974): Q, A, Kf, M, K, Fe-sulfides	–	–	–
	2–7	A		**Q,** A, Kf, M, Ge?, Ch	**S and/or M/S, V and/or HIV (HIS), M,** K, Q, A	**S and/or M/S, V?, M,** K
	7–14	C1		**Q, Gy,** A, Kf, M, Ch, K?	**S and/or M/S, V and/or HIV (HIS), M,** K, Q	**S and/or M/S, V?, M,** K
	14–30	C2		**Q,** Gy, Kf, A, Ch, M,	**S and/or M/S, M,** V?, K, Q, A, Kf	**S and/or M/S, M,** K
	30–60	C3		**Q,** Gy, A, Ch, M, Kf, J?	**S and/or M/S, M,** V?, K, Q	**S and/or M/S,** M, K
	60–75	C4		**Q,** Gy, Kf, A, Ch, M, Py, J	**M, S and/or M/S, K,** V?, Q, A	**S and/or M/S, and/or M/V, M,** K
W1	0–1	Oi	Main minerals according to Uzarowicz et al. (2008): Q, Ch, M, A, Pa, Kf, Py	–	–	–
	1–4	Oe		–	–	–
	4–9	A1		**Q, Ch,** A, Kf, M, Pa, K, Gy, J?	**M, Ch,** B, K, S and/or M/S, Q, A	**S and/or M/S, M, Ch,** B, K, V?, Q
	9–10	A2		**Q, Ch,** M, A, Kf, Pa, K, J?	**M, Ch,** B, K, S and/or M/S	–
	10–45	C		**Q, M, Ch, Kf,** A, Pa, K, J	**M,** B, Ch, S and/or M/S, K	**S and/or M/S, M,** Ch, B, K
W2	0–1	Oi		–	–	–
	1–4	A		**Q, Ch,** A, M, Pa, Kf, K?	**Ch, M,** B, K, S and/or M/S, Q, A	**S and/or M/S, Ch, M,** B, K, Q
	4–15	AC		**Q, Ch,** A, M, Pa, Kf, K	**Ch, M,** B, K, S and/or M/S, Q	**S and/or M/S, Ch, M,** B, K, Q
	15–30	C1		**Q, Ch,** A, M, Pa	**Ch, M, B,** S and/or M/S, K, Q	–
	30–35	C2		**Q, A,** Ch, M, Pa	**Ch, M, B,** K, S and/or M/S, Q, A	**S and/or M/S, Ch, M,** B, K, Q
	35–86	C3		**Q, Ch,** A, M, Pa, K, J	**Ch, M, B,** K, S and/or M/S, Q	**S and/or M/S, Ch, M,** B, K, Q, A
	86–112	C4		**Q, Ch,** A, M, Gy, Pa, K?	**Ch, M, B,** K, S and/or M/S, Q	**S and/or M/S, Ch, M,** B, K, Q

Minerals: A—albite, B—Na-mica (brammalite), C—calcite, Ch—chlorite, Do—dolomite, Fs—feldspar (not identified), Ge—goethite, Gi—gibbsite, Gy—gypsum, He—hematite, HIS—hydroxy-interlayered smectite, HIV—hydroxy-interlayered vermiculite, J—jarosite, K—kaolinite, Kf—K-feldspar, M—K-mica (muscovite or so-called illite in clay fraction), M/S—mixed-layer mica/smectite, M/V—mixed-layer mica/vermiculite, Ma—marcasite, Pa—paragonite, Py—pyrite, Q—quartz, S—smectite, Si—siderite, V—vermiculite.
Predominant minerals are in bold.
– not determined.

stage of the sulfuricization process (e.g. Fanning et al., 1993). In young technogenic soils from Trzebinia and Rudki (T1, T2, and R2 profiles), the pH_{H2O} value dropped below 3 in certain soil layers (Table 2). The highest acidification occurred in the layers in which vast amounts of sulphides were present (as indicated by the observation made during the field work). R1 profile from Rudki had near neutral reaction (pH_{H2O} from 7.2 to 7.4, Table 2) in spite of vast amounts of sulphides. A high pH value in that case was caused by the high content of carbonates (mainly dolomite) occurring as primary minerals in the post-flotation sludge (C2 horizon, Table 3), or added to the soil during reclamation (A and C1 horizons). The investigated soils contained large amounts of trace elements (Uzarowicz, 2011).

3.2. Mineral composition of parent materials and bulk mineralogy of soils

The soils investigated were composed of various post-mining wastes, thus vary in mineral composition. The common feature of all of the soils studied was the presence of sulphide minerals and/or products of their weathering. Information on the mineral composition of mine wastes, which can by assigned as parent rock for the soils studied, is crucial for the determination of mineral transformations in the soils. Such data involving soils investigated are available elsewhere (Table 3). Minerals inherited from parent rock predominate in all of the examined bulk soil samples (<2 mm, Table 3). Secondary minerals, represented mainly by sulphate minerals and iron oxides, were present in smaller amounts.

Inherited quartz and feldspars predominated in both studied soil profiles (T1 and T2) from Trzebinia. Kaolinite, which was one of the most important minerals in layers containing large amounts of clay fraction (e.g. in C2 horizon of T1 profile, Table 3), was also a common mineral in these soils. T1 and T2 profiles contained inherited mica (muscovite), small amounts of chlorite, and poorly weathered iron sulphides. In addition to the minerals mentioned above, also secondary sulphates (gypsum and jarosite), as well as iron oxides were present.

R1 profile from Rudki developed on former flotation tanks, and was composed of two different materials. The lower part of the profile (C2 horizon) was composed of post-flotation sludge, mainly consisting of inherited dolomite and secondary gypsum (Table 3). Inherited minerals in C2 horizon were also iron sulphides (marcasite and pyrite) and trace amounts of siderite. The upper part of R1 profile (A and C1 horizons) was made of loamy material deposited on post-flotation sludge during reclamation. It mainly consisted of inherited minerals, such as quartz, iron oxides (goethite and hematite), mica (muscovite), chlorite, kaolinite, gibbsite, dolomite, and small amounts of iron sulphides. Gypsum is the main secondary mineral.

R2 profile from Rudki developed on the former mine waste dump “Serwis”. The main mineral present in this profile was inherited quartz (Table 3). There were also smaller amounts of other inherited minerals, such as feldspars (plagioclases and potassium feldspar), mica (muscovite), chlorite, kaolinite, and iron sulphides. Secondary sulphates (gypsum and jarosite) and iron oxides were also present.

Both of the studied soil profiles from Wieściszowice (W1 and W2 profiles) contained mainly inherited quartz, chlorite, muscovite, paragonite, and feldspars (Table 3). Secondary minerals were represented by smaller amounts of gypsum, jarosite, and iron oxides.

3.3. Iron sulphide transformations and the development of sulphates and iron oxides

Sulphide minerals occurred in various amounts in all of the soils investigated. It was confirmed by field observations (findings of sulphides in rock fragments from soils), as well as optical microscopic examination and studies in SEM (Figs. 1, 2, 3 and 4). In comparison with other minerals, sulphides were present in scarce amounts, thus making it impossible to determine their presence with the use of XRD method in most cases. Relatively large amounts of sulphide minerals were typical of soil profiles from Trzebinia (T1 and T2) and Rudki (R1 and R2) (Figs. 1 and 2). Several centimetre large rock fragments composed of sulphides were often found during field work in the profiles mentioned (not shown). Sulphide minerals in soil profiles from Wieściszowice (W1 and W2) were present in scarce amounts, mostly in the form of several millimetre grains occurring inside rock or mineral fragments (Fig. 3).

Sulphides present in young soils from Trzebinia and Rudki were poorly weathered. Weathering of sulphides involved mostly surfaces of crystals and cracks in grains, where layers composed of “massive” iron oxides developed (Figs. 1 and 2). Similar features of pyrite weathering were found by other authors (e.g. Dixon et al., 1982; Lu et al., 2005). In soils developed on mine spoils in Wieściszowice, the progress of sulphide weathering, related to the long duration of the process, was remarkably more advanced than in young soils. Sulphides in soils from Wieściszowice were almost entirely, or sometimes entirely transformed into secondary minerals (Fig. 3). Weathered zones occurring in sulphide grains consisted of numerous layers, visible in back-scattered electron (BSE) images in SEM as alternating light-grey and dark-grey layers concentrated around the remnants of sulphide grains (Fig. 3). Secondary weathering rims consisted mainly of oxygen, iron, and sulphur. Therefore, they most likely constituted a mixture of “massive” iron oxides and sulphates (Fig. 3). The occurrence of the rims seems to be a common feature in weathered mine wastes containing sulphides (e.g. Burlak et al., 2010).

Transformations of iron sulphides are among the most important mineral alterations occurring in the technogenic soils studied and influencing chemical properties (e.g. pH) of the soils. It is in accordance

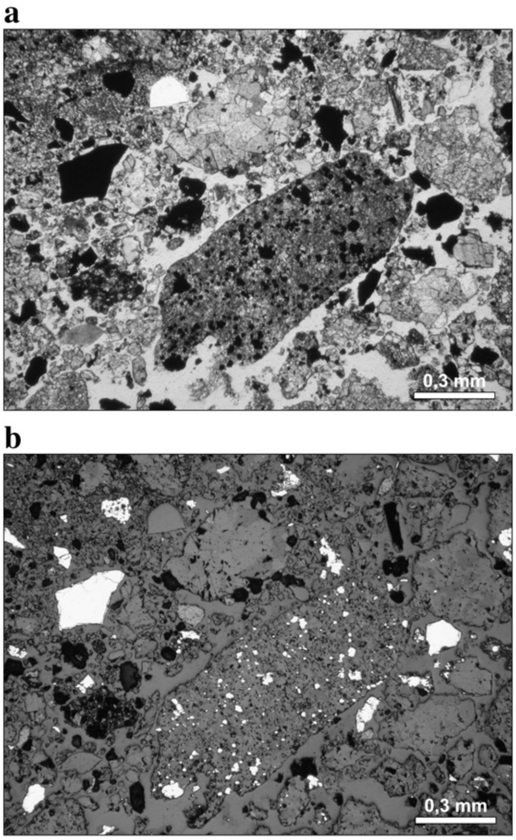


Fig. 1. Poorly weathered iron sulphides (white crystals in photo b) surrounded by soil material composed mainly of carbonates from post-flotation sludge from Rudki (R1 profile, C2 horizon); a—transmitted light, plane polarized light; b—plane reflected light.

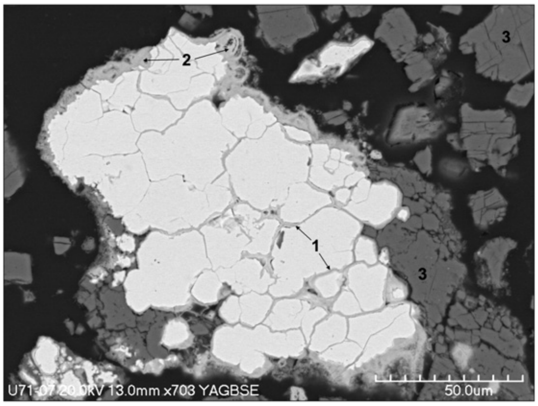


Fig. 2. Partly weathered iron sulphide grain (white colour), secondary iron oxides as veins (1) and coatings (2), and dolomite (3) from the post-flotation sludge from Rudki (R1 profile, C2 horizon); back-scattered electron image in SEM.

with other studies concerning weathering processes of mine spoils containing sulphides (e.g. Dixon et al., 1982; Grube et al., 1982; Skawina, 1959a,b; Strzyszcz, 1978).

In addition to the development of "massive" iron oxides developing within sulphide grains, porous iron oxides also crystallized in the soils investigated. They formed individual, irregular aggregates developed in the vicinity of sulphides (Fig. 4). A relatively large agglomeration of porous oxides occurred in the extremely acid R2 profile from Rudki. Those aggregates consisted of oxygen and iron, but also contained certain amounts of aluminium (Fig. 4). Therefore, they most likely comprised a mixture of amorphous or poorly crystalline iron and aluminium oxides. The development of such mixtures in acid soils influenced by acid mine drainage was documented by Šucha et al. (2002).

Sulphate ions originated in the process of weathering of sulphides. They crystallized in the soils studied as sulphate minerals, mainly represented by gypsum and jarosite group minerals (Figs. 5 and 6). These minerals are common secondary minerals, e.g. in acid sulphate soils (Wagner et al., 1982), as well as in lignite overburdens containing sulphides (Dixon et al., 1982). Gypsum occurred in all of the soils investigated but its amounts were varied. Relatively large amounts of gypsum were present in young soils from Trzebinia and Rudki. In old soils from Wieściszowice, gypsum was a rather rare mineral. Certain soil horizons (layers), e.g. in C4 horizon from W2 profile from Wieściszowice (Table 3), contained larger amounts of the mineral. Gypsum occurred as subhedral (rarely euhedral), prismatic crystals (Fig. 5). Tabular crystals of gypsum, however, were also present in the soils investigated (not shown).

Jarosite group minerals were identified in all of the soils studied, except for R1 profile from Rudki characterized by near neutral reaction (Table 3). In comparison with other minerals, jarosite group minerals were a minor constituent in the soils investigated, as indicated by not very intense peaks in XRD patterns (not shown), and

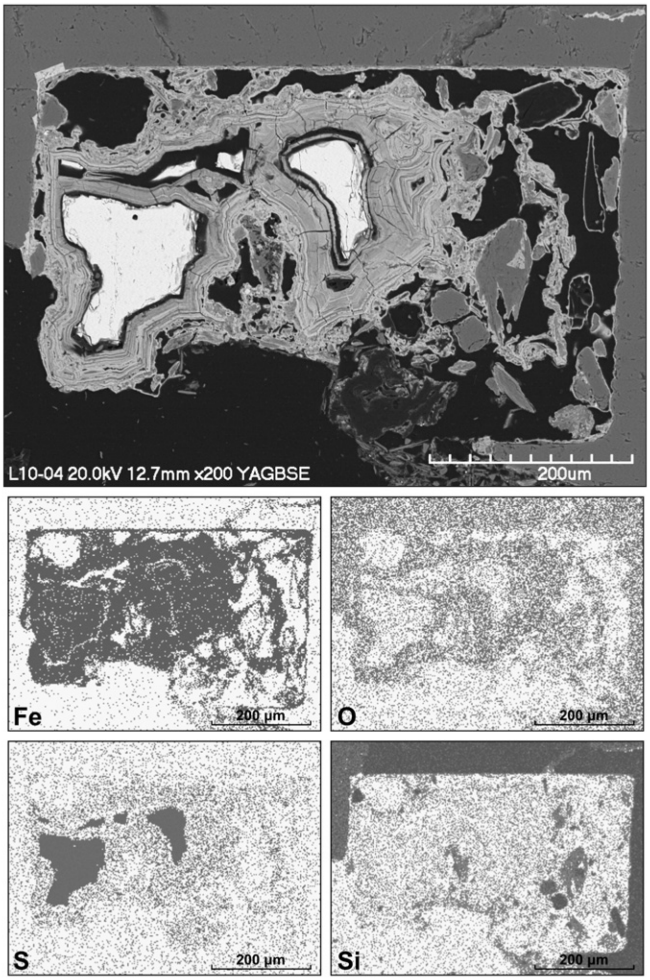


Fig. 3. Strongly weathered sulphide crystal partly replaced by secondary iron oxides and sulphate minerals from W1 profile, A2 horizon; back-scattered electron image in SEM and elemental maps for the selected elements.

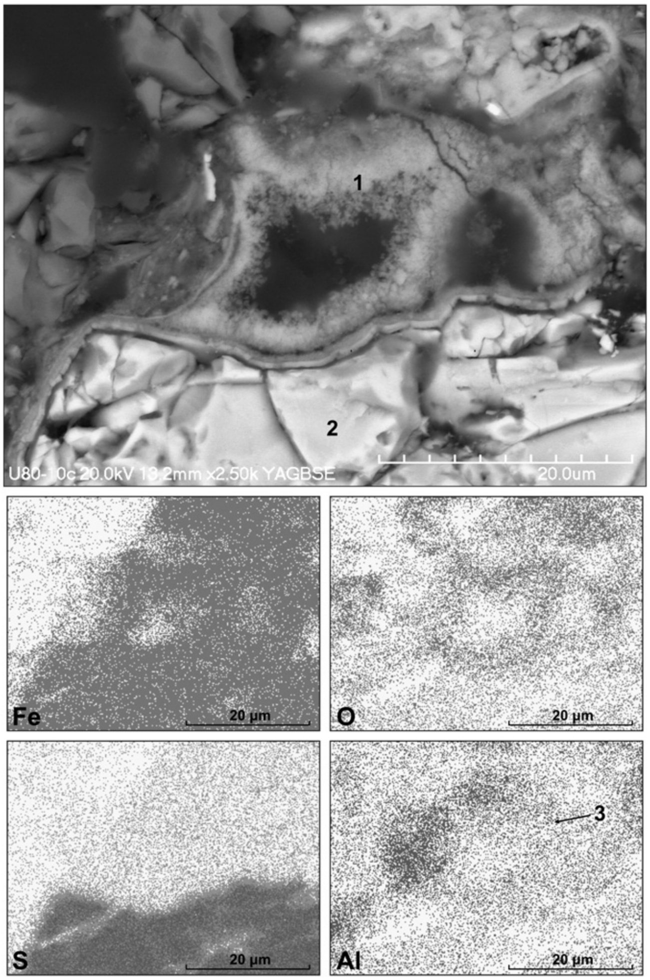


Fig. 4. Porous aggregates of iron oxides (1) crystallized in the vicinity of iron sulphide (2) and containing some amounts of Al (3) from R2 profile, C4 horizon; back-scattered electron image in SEM and elemental maps for the selected elements.

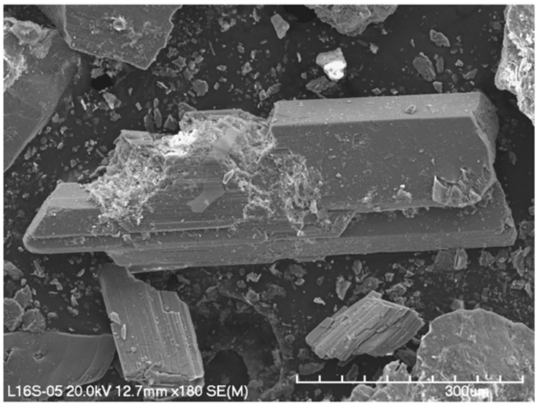
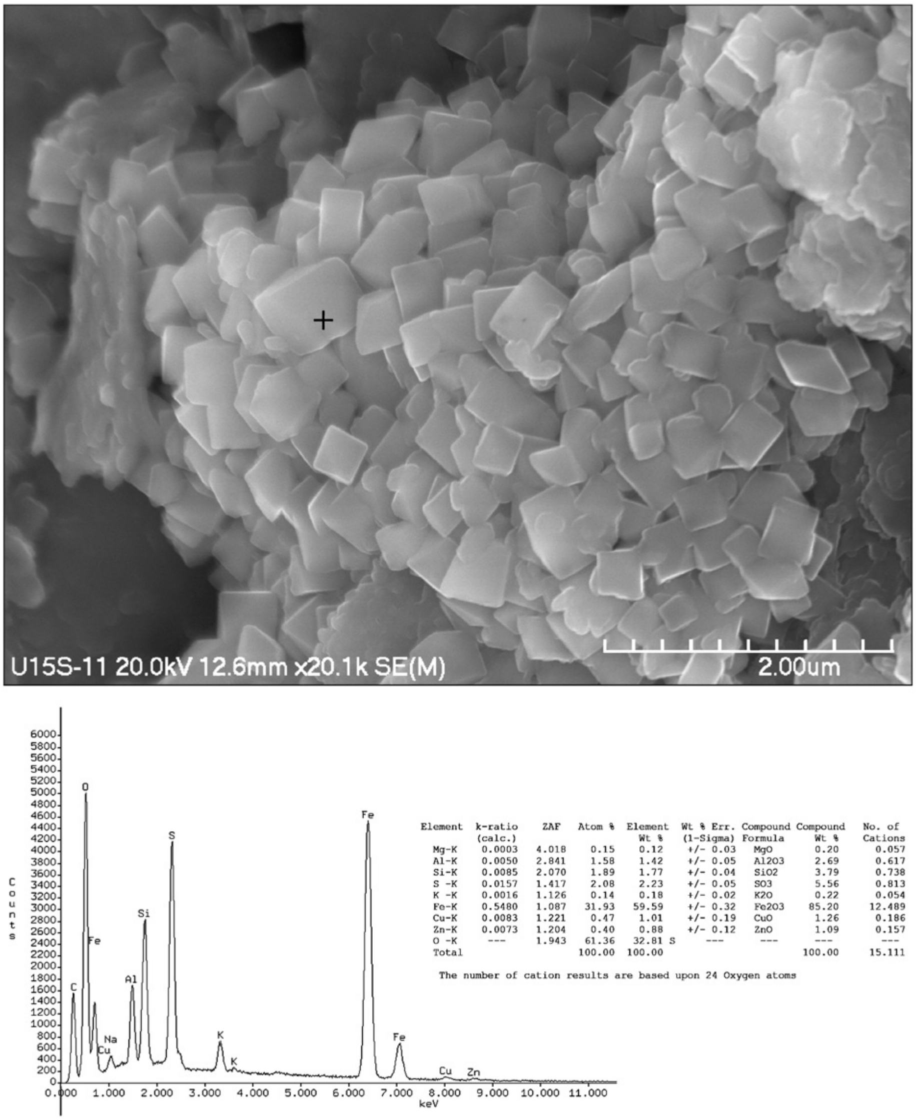


Fig. 5. Subhedral, prismatic crystal of gypsum from W2 profile, C4 horizon; secondary electron image in SEM.

sparse observations in SEM. Most jarosite specimens found in the soils during the observations in SEM were about 1 μm large (along the longest dimension) nearly isometric crystals (Fig. 6). Similar jarosites were documented in many weathered materials containing oxidized sulphides (e.g. Dixon et al., 1982; Lintnerová et al., 1999; Wagner et al., 1982). The best developed cubic-shaped jarosite crystals were found in the extremely acid Trzebinia and Rudki soils (Fig. 6). Cubic shape is the most common habit of this mineral (Mees and Stoops, 2010). The presence of cubic jarosite crystals may also suggest that they are pseudomorphs after pyrite, which was discussed in the literature (e.g. Dixon et al., 1982; Doner and Lynn, 1989, and the literature cited therein; Poch et al., 2009).

The EDS analyses performed during SEM observations were not very conclusive in distinguishing the types of jarosite group minerals. They might include jarosite $KFe_3[(OH)_6|(SO_4)_2]$, natrojarosite $NaFe_3[(OH)_6|(SO_4)_2]$, and/or hydronium jarosite $(H_3O)Fe_3[(OH)_6|(SO_4)_2]$—the most common jarosites occurring in nature (Doner and Lynn, 1989; Kubisz, 1970). A high content of oxygen in the chemical composition of the analysed crystals (Fig. 6), indicating indirectly the presence of water in the structure, showed that hydronium jarosite may be an important mineral phase. The formation of alkali-deficient jarosites, such as hydronium jarosite, takes place in nature, i.e. in mine spoils containing sulphides (e.g. Basciano and Peterson, 2007), as well as was evidenced in laboratory conditions (e.g. Kubisz, 1970). A high content of iron in the cubic crystals observed indicates that these



```
Element  k-ratio   ZAF   Atom %  Element  Wt % Err. Compound Compound   No. of
         (calc.)                   Wt %  (1-Sigma) Formula     Wt %    Cations
  Mg-K   0.0003   4.018    0.15    0.12   +/- 0.03  MgO         0.20     0.057
  Al-K   0.0050   2.841    1.58    1.42   +/- 0.05  Al2O3       2.69     0.617
  Si-K   0.0085   2.070    1.89    1.77   +/- 0.04  SiO2        3.79     0.738
  S -K   0.0157   1.417    2.08    2.23   +/- 0.05  SO3         5.56     0.813
  K -K   0.0016   1.126    0.14    0.18   +/- 0.02  K2O         0.22     0.054
  Fe-K   0.5480   1.087   31.93   59.59   +/- 0.32  Fe2O3      85.20    12.489
  Cu-K   0.0083   1.221    0.47    1.01   +/- 0.19  CuO         1.26     0.186
  Zn-K   0.0073   1.204    0.40    0.88   +/- 0.12  ZnO         1.09     0.157
  O -K    ---     1.943   61.36   32.81 S   ---      ---        ---       ---
  Total                  100.00  100.00                       100.00    15.111

   The number of cation results are based upon 24 Oxygen atoms
```

Fig. 6. Pseudocubic sulphate crystals, most likely of jarosite group from T2 profile, C4 horizon; secondary electron image in SEM and the EDS chemical analysis; the cross indicates the point of EDS analysis; Si, Al, and also part of K and Na in the analysis come from aluminosilicates occurring below the sulphates analysed.

phases may be a mixture of sulphates and iron oxides. They may also constitute a mixture of sulphates, including unrecognized iron sulphates, documented e.g. in the lignite mine spoils (Dixon et al., 1982).

3.4. Phyllosilicate transformations and clay mineral formation

In soils developed on mine spoils in Trzebinia (T1 and T2 profiles), the predominant clay mineral was kaolinite (identified by the presence of ~0.7 and 0.358 nm basal reflections in air-dry samples) and mica (illite-type mineral, ~1.0 nm basal reflection which did not change position in any diagnostic tests) (Fig. 7, Table 3). That mineral were phases inherited from parent rock (Twardowska et al., 1988; Strzyszcz, 1989; Bzowski and Strzyszcz, 1993; Table 3). Owing to the SEM-EDS analyses, dioctahedral (Al- and Si-rich) K-mica (so-called illite) was determined as the main mica mineral occurring in the soils. In the clay fraction of the soils, quartz occurred in minor amounts. In the XRD pattern of glycerol-treated Mg-saturated clay samples, there was no well-defined reflection near 1.8 nm (Fig. 7), thus the presence of smectite was not confirmed. In the XRD pattern of air-dried Mg-saturated clay, reflections ~1.1–1.2 nm can be seen (Fig. 7). It may indicate the presence of certain interstratified clay minerals, e.g. mica/smectite or mica/vermiculite. This mineral phase is most likely a secondary clay mineral developing at the expense of mica in an extremely acid soil environment.

In the clay fraction of the nearly neutral soil profile R1 developed on flotation tanks in Rudki, the following minerals predominated: kaolinite (~0.7 and 0.358 nm reflections) and mica (~1.0 nm basal reflection) (Fig. 8, Table 3), which most likely were inherited mineral phases (Skawina et al., 1974). In both studied soils from Rudki (R1 and R2), mica was represented by Al- and Si-rich K-mica (so-called illite). In the XRD patterns of clay fraction from R1 profile, the presence of swelling clay minerals was hardly evidenced, as in the XRD pattern of glycerol-treated Mg-saturated clay from A horizon only little background uplift could be seen near 1.8 nm (Fig. 8). There was a slight quantitative difference in contents of mica and kaolinite between the topsoil (A and C1 horizons) and the subsoil (C2 horizon) taking into consideration the intensities of 001 and 002 reflections of mica and kaolinite in XRD patterns (Fig. 8). It was because they represented two different anthropogenic materials. In the subsoil, mica was relatively more abundant than in the topsoil (Fig. 8). In the clay fraction of the topsoil, lower amounts of goethite, hematite, and feldspar occurred, and in the subsoil, apart from mica and kaolinite, also small amounts of gibbsite, quartz, and feldspar were present. The minerals were most likely inherited from parent rock, as they are common mineral constituents of mine spoils coming from the abandoned mine in Rudki (Skawina et al., 1974).

In the clay fraction of the acid R2 profile from Rudki, apart from K-mica and kaolinite, which most likely were inherited minerals, also large amounts of swelling minerals, which probably represented secondary phases, occurred. Smectite (reflection ~1.8 nm in the glycerol-treated Mg-saturated sample) and vermiculite (reflection ~1.45 nm in the glycerol-treated Mg-saturated sample, and the disappearance of that reflection in the heated sample) could be seen in the XRD patterns (Fig. 9). The ~1.45 nm reflection of vermiculite was well-defined in the less acid topsoil (A and C1 horizons) rather than in the extremely acid subsoil (C2, C3, and C4 horizons) (Fig. 9). The presence of mixed-layer clay minerals was likely, as the reflections of smectite were very broad, and the background uplift could be seen in the low °2Θ region in the XRD pattern of Mg- and glycerol-saturated clays (Fig. 9). The incomplete collapse to 1.0 nm after heating (clays from A and C1 horizons) (Fig. 9) indicated the presence of interlayers (e.g. hydroxy-Al interlayers) within the vermiculite and/or smectite structure (Barnhisel and Bertsch, 1989). The data suggest that the formation of interlayers is pH-dependent. The pH dependency of hydroxy-interlayer development was documented in podzols (e.g. Bain et al., 1990; Skiba, 2007). In the soils studied, interlayers develop at pH around 4.3-4.4 (Table 2). Furthermore, the formation of vermiculite and smectite in the acidic range of pH also seems to be dependent on the degree of acidification, as the mineral composition of clay fractions from the topsoil and the subsoil of R2 profile showed slight differences (Fig. 9). That thesis can be supported by the fact that the whole R2 profile was built of uniform, loamy and brown material, and the main difference between the topsoil and the subsoil was the pH (Table 2). Vermiculite in R2 profile formed when pH was around 4.3–4.4, whereas smectite might form not only in such conditions, but also in extremely acid soil horizons ($pH<3$). Both smectite and vermiculite in R2 profile were most likely products of mica weathering.

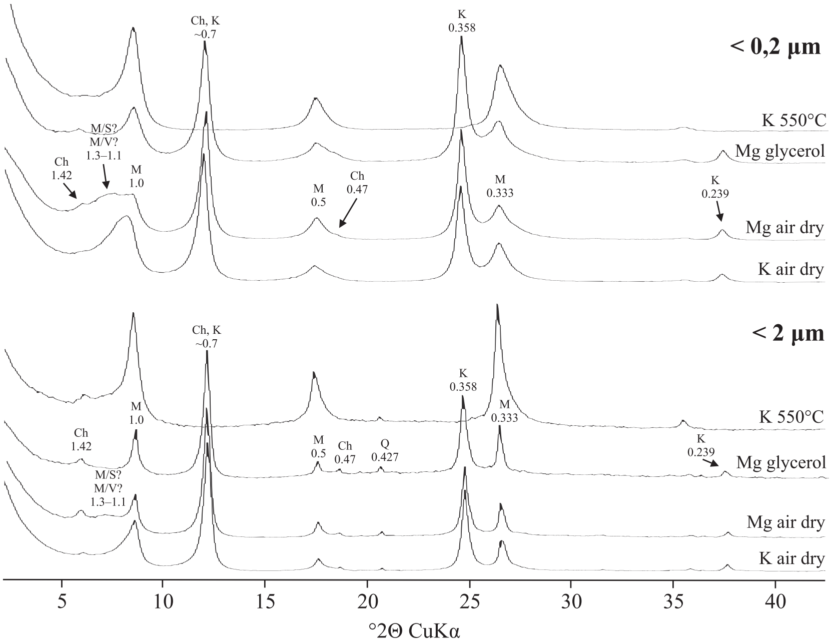


Fig. 7. Mineral composition of soil clay fractions (<0.2 and <2 µm) from T2 profile, C2 horizon. The *d* values in nm. Minerals as in Table 3.

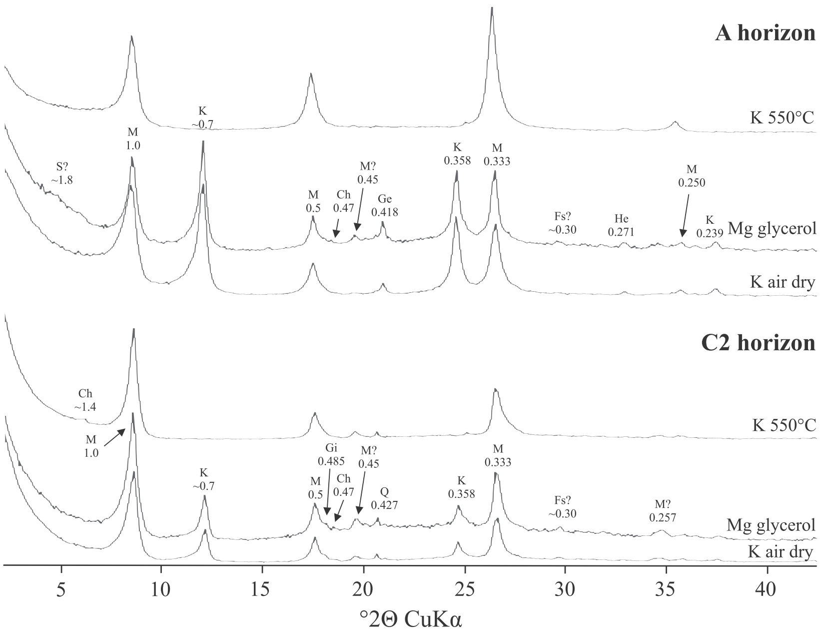


Fig. 8. Mineral composition of soil clay fraction (<2 µm) from R1 profile. The *d* values in nm. Minerals as in Table 3.

Preliminary investigations concerning phyllosilicate transformations in technogenic soils from Wieściszowice (Uzarowicz et al., 2008) showed that the soil clay fraction was predominated by inherited minerals (trioctahedral chlorite, as well as dioctahedral K-mica and Na-mica) (Fig. 10). Apart from the above mentioned minerals, also smectite and kaolinite, which most likely were secondary minerals, occurred (Fig. 10). Also secondary vermiculite may be present, but it was difficult to confirm that relying on the XRD patterns because of the chlorite and vermiculite ~1.4 nm reflection overlapping. Smectite was more abundant in the <0.2 µm fraction than in the <2 µm fraction. The mineral may occur as a discrete phase, but the broad ~1.7 nm reflection in XRD patterns of ethylene-glycol treated clays indicated that smectite may also be present as a mixed-layer mineral.

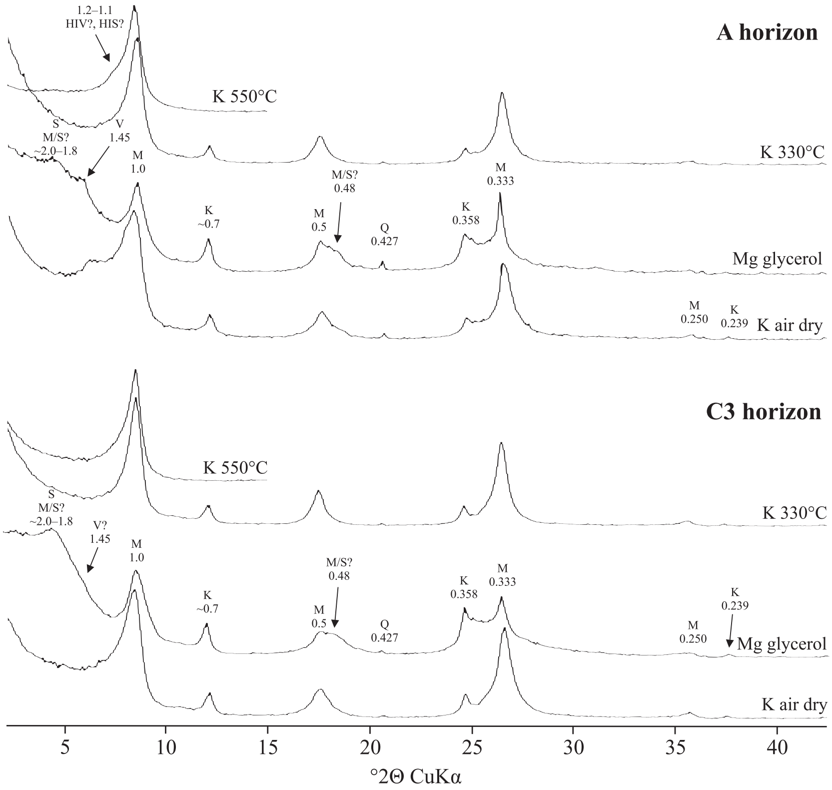


Fig. 9. Mineral composition of soil clay fraction (<2 µm) from R2 profile. The *d* values in nm. Minerals as in Table 3.

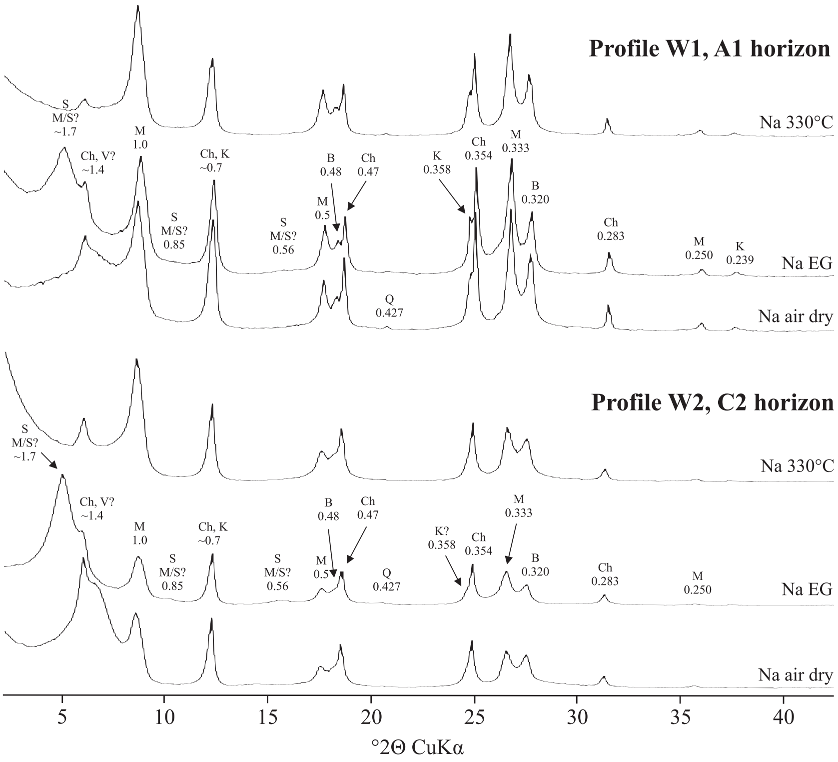


Fig. 10. Mineral composition of soil clay fraction (<0.2 μm) from W1 and W2 profiles. The *d* values in nm. Minerals as in Table 3.

The results obtained concerning mineral transformations in the clay fraction indicate that in the youngest soils investigated (profiles T1 and T2 from Trzebinia), phyllosilicates transformations were hardly visible. It is supported by scarce amounts of swelling phases in soil clays. Moreover, the mineral composition of the clay fraction in soils from Trzebinia did not vary between the soil profiles. In the acid soil profiles from Rudki (R2) and Wieściszowice (W1 and W2), phyllosilicate transformations were more advanced. Certain differences also occurred in mineral composition between distinguished horizons in the latter soils. The differences were most likely the result of diverse chemical properties of the soil horizons.

The results also suggest that acid reaction in the technogenic soils investigated favours transformations of primary phyllosilicates into swelling minerals. The most abundant product of these transformations in the soils investigated was smectite occurring as a discrete mineral or a mixed-layer mineral. Lower amounts of vermiculite and/or hydroxy-interlayered vermiculite also developed. The formation of swelling clay minerals was confirmed by the occurrence of such minerals in all of the acidic soils studied (T1, T2, R2, W1, and W2 profiles) regardless of the age, and, on the other hand, by the absence of swelling minerals in soil with near neutral reaction (R1 profile). Swelling minerals commonly develop in acid soil environments, e.g. in podzols and soils influenced by acid sulphate weathering (April et al., 2004; Borchardt, 1989; Carnicelli et al., 1997; De Kimpe and Miles, 1992; Douglas, 1989; Grube et al., 1982; McDaniel et al., 1995; Righi et al., 1997; Ross et al., 1982; Skiba, 2007; Šucha et al., 2002). In the soils studied, swelling minerals most likely develop at the expense of mica and chlorite, as it is not justified to assume that smectite, vermiculite, HIV, and HIS are the products of weathering of one mineral (mica or chlorite) exclusively. Larger amounts of swelling minerals occurred in the <0.2 μm fraction than in <2 μm fraction of all of the soils studied (Figs. 7, 9, and 10). Therefore, the minerals most likely develop as a result of strong disintegration of mica and chlorite crystals along with chemical transformations (e.g. partial hydration of chlorite, loss of interlayer K and a decrease in layer charge in the process of mica weathering) in the acidic soil environment. It is in accordance with the generally accepted view (e.g. Borchardt, 1989; Aoudjit et al., 1996; Reid-Soukup and Ulery, 2002, and the literature cited therein).

3.5. Forms of Fe, Al, and Si in soils

Extracted forms of Fe, Al, and Si vary both between and within individual soil profiles. This results from the fact that the profiles represent technogenic soils composed of diverse industrial materials randomly deposited on mine spoils.

Although it is well known that the reagents used in extractions (dithionite, oxalate, and pyrophosphate) may dissolve iron-containing minerals other than the iron oxides required (Loeppert and Inskeep, 1996 and the literature cited therein), however, little is known about the possible effect of reagents used on dissolution of iron sulphides or other Fe-containing minerals present in the soils studied (e.g. siderite). For instance, Hita and Torrent (2005) claimed that dithionite–citrate–bicarbonate extractions dissolves pyrite to a negligible extend.

The soils studied contained large amounts of Fe (Table 4). For most of the soils studied (except for soils from Rudki in which vast amounts of inherited goethite and hematite occurred, Table 3) it can be assumed that "free" iron was released to the soils in the process of iron sulphide oxidation, then hydrated and transformed into poorly crystalline oxyhydroxides (e.g. ferrihydrite), and subsequently transformed into well-crystallized iron oxides, e.g. goethite. It is a common process in soils and weathering zones of temperate regions (e.g. Schwertmann, 2008). The thesis can be supported by the absence or scarce amounts of inherited iron oxides in soils from Trzebinia and Wieściszowice, as confirmed by the mineralogical study (Figs. 2, 3, and 4, and Table 3) and other investigations (e.g. Strzyszcz, 1989; Twardowska et al., 1988; Uzarowicz et al., 2008).

The relation between the amounts of dithionite and oxalate-extractable Fe is a commonly used parameter showing the transformations of Fe oxides in the course of soil-forming processes (Cornell and Schwertmann, 2003). The Fe_{dith}/Fe_{ox} ratio in most of the

Table 4
Forms of Fe, Al, and Si in the soils investigated.

Profile	Depth	Horizon	Form of Fe, Al, and Si (g/kg)						$(Al_{ox}–Al_{pyr})/Si_{ox}$	Fe_{dith}/Fe_{ox}
			Fe_{dith}	Fe_{ox}	Fe_{pyr}	Al_{ox}	Al_{pyr}	Si_{ox}		
T1	0–10	C1	12.5	17.4	3.6	0.6	0.8	0.3	−0.9	0.7
	10–35	C2	11.0	12.8	1.7	0.9	1.3	0.2	−1.7	0.9
T2	0–40	C1	8.6	9.7	1.9	0.6	0.8	0.2	−0.9	0.9
	40–76	C2	26.3	15.9	1.2	1.2	1.0	0.4	0.4	1.6
	76–98	C3	26.7	20.9	1.6	0.8	1.0	0.5	−0.3	1.3
	98–105	C4	53.0	37.7	2.6	0.2	1.0	0.1	−6.7	1.4
R1	0–1	Oi	–	–	–	–	–	–	–	–
	1–3	A	113.7	1.1	0.2	0.1	1.1	0.1	−9.7	101.0
	3–30	C1	94.1	1.0	0.4	0.1	1.8	0.1	−12.4	90.8
	30–95	C2	40.6	47.9	0.2	0.2	0.6	0.2	−1.8	0.8
R2	0–2	Oi	–	–	–	–	–	–	–	–
	2–7	A	47.8	8.8	2.4	4.2	3.4	0.7	1.1	5.4
	7–14	C1	37.9	9.3	1.9	6.0	4.1	1.5	1.3	4.1
	14–30	C2	52.9	23.0	4.5	1.0	3.9	0.3	−10.9	2.3
	30–60	C3	45.4	19.0	6.0	1.3	4.4	0.3	−9.4	2.4
	60–75	C4	32.9	9.6	5.0	1.7	4.2	0.4	−5.6	3.4
W1	0–1	Oi	–	–	–	–	–	–	–	–
	1–4	Oe	–	–	–	–	–	–	–	–
	4–9	A1	62.3	19.2	5.4	1.7	2.0	0.3	−1.4	3.2
	9–10	A2	91.5	28.1	4.9	1.1	1.7	0.4	−1.3	3.3
	10–45	C	46.6	27.0	1.5	0.6	1.4	0.2	−3.4	1.7
W2	0–1	Oi	–	–	–	–	–	–	–	–
	1–4	A	21.7	14.3	1.3	0.4	1.2	0.2	−4.5	1.5
	4–15	AC	22.1	13.5	1.2	0.5	1.2	0.2	−3.0	1.6
	15–30	C1	24.8	18.2	1.2	0.6	1.4	0.6	−1.3	1.4
	30–35	C2	18.5	17.3	0.3	0.3	0.9	0.3	−2.2	1.1
	35–86 white spots	C3	4.2	2.7	0.3	0.5	0.8	0.4	−0.7	1.5
	35–86 rusty trails	C3	64.2	42.8	1.0	0.7	0.9	1.1	−0.2	1.5
	86–112	C4	7.0	8.3	0.1	0.1	0.7	0.1	−6.1	0.8

soil profiles studied was around 1 and rarely exceeded 1.5 (Table 4). This suggests that well-crystallized Fe oxides only slightly predominate over poorly crystalline Fe oxides. The highest value of the Fe_{dith}/Fe_{ox} ratio was typical of old soils from Wieściszowice (represented by the best developed W1 profile, in which the ratio exceeded the value of 3) and Rudki (Table 4). In the case of soils from Wieściszowice, the high value of the Fe_{dith}/Fe_{ox} ratio was most likely the effect of the development of well-crystallized iron oxides during iron sulphide oxidation, unlike the soils from Rudki (R2 profile and the upper part of R1 profile), in which the high value of the ratio, exceeding the value of 100 in A horizon of R1 profile, was caused by the presence of goethite and hematite inherited from the parent material (Table 3). In certain soil samples, i.e. in the very weakly developed (young) T1 profile, in the post-flotation sludge (C2 horizon in R1 profile) and in the lowermost part of the profile W2, the Fe_{dith}/Fe_{ox} ratio was below 1, which suggests that other Fe minerals (e.g. siderite and chlorite), not considered as “free” Fe, were attacked during oxalate extraction (e.g. Schwertmann, 2008).

The results obtained indicate that if the parent material contain no or very little inherited iron oxides (i.e. the main source of “free” Fe are oxidized iron sulphides), the Fe_{dith}/Fe_{ox} ratio may be a good indicator of the advancement of weathering (soil-forming) processes occurring in technogenic soils developed on mine spoils containing iron sulphides (the higher the ratio, the more advanced the weathering and soil-forming processes). The results presented in the paper are in accordance with the studies by Hita and Torrent (2005), which investigated soils containing fresh pyritic and sphaleritic sludge. Hita and Torrent (2005) stated that in the first two or three years of sulphide weathering in soils, the content of newly formed poorly crystalline Fe oxides increased. The phases may subsequently transform into well-crystallized Fe oxides as the process of sulphide oxidation proceeds.

The highest values of Fe_{pyr} occurred in the uppermost parts of the soils investigated, and were related to the high content of soil organic matter (Table 4).

Values of the $(Al_{ox}–Al_{pyr})/Si_{ox}$ ratio were negative in most of the soils samples studied. Such feature indicates unfavourable conditions for the development of Al-rich amorphous phases (e.g. allophane) expected to develop in acid soils with the $(Al_{ox}–Al_{pyr})/Si_{ox}$ ratio close to 2 (Parfitt and Henmi, 1982). The positive value of the $(Al_{ox}–Al_{pyr})/Si_{ox}$ ratio is typical of the upper part of the R2 profile (A and C1 horizon), and equals 1.1 and 1.3, respectively. This (together with the pH 4.3–4.4, Table 2) suggests the occurrence of conditions similar to those favourable for the development of Al-rich amorphous phases. XRD analysis showed that in A and C1 horizons of R2 profile, hydroxy-interlayers, which were most likely Al-hydroxy polymers, may develop (Fig. 9). Conditions favourable for the development of both Al-rich amorphous phases and Al-hydroxy interlayers were evidenced by a relatively high quantity of Al_{ox} (in comparison with other soil samples) (Table 4), indicating an important role of poorly crystalline Al compounds in the chemistry and mineralogy of the upper part of the R2 profile, which is connected with the pH of soil (e.g. Parker, 2005).

3.6. Selected problems with the classification of technogenic soils developed on mine spoils containing iron sulphides

All of the soils studied were classified according to the World Reference Base for Soil Resources (IUSS, 2006) as variants of *Spolic Technosols* (Table 5) because of the presence of artefacts (which are industrial wastes) occurring in the uppermost 100 cm layer of the soils. Technogenic soil layers (specified in soil descriptions as C horizons), with acid reaction and yellowish colours (hue of 2.5Y and chroma of 6 or more), have the features of *thionic* horizon (IUSS, 2006) (pH less than 4.0, thickness of more than 15 cm, presence of jarosite) in most of the soil profiles. Although one of the diagnostic criteria of *thionic* horizon is the occurrence of sulphates, the description of the horizon in WRB does not mention the possibility of the presence of weathered sulphide minerals. Such feature was documented in the soils studied. The authors suggest that the

Table 5
Present and proposed classification of the soils investigated.

Profile	WRB present	WRB proposed	Soil taxonomy present	Soil taxonomy proposed
T1	Spolic Technosol (Toxic, Humic, Skeletic)	Spolic Technosol (Hyperthionic, Toxic, Humic, Skeletic)	Typic Udorthent	Sulfic Udorthent
T2	Spolic Technosol (Toxic, Humic)	Spolic Technosol (Hyperthionic, Toxic, Humic)	Typic Udorthent	Sulfic Udorthent
R1	Spolic Technosol (Calcaric, Toxic)	Spolic Technosol (Calcaric, Toxic)	Typic Udorthent	Typic Udorthent
R2	Spolic Technosol (Toxic)	Spolic Technosol (Hyperthionic, Toxic)	Typic Udorthent	Sulfic Udorthent
W1	Spolic Technosol (Skeletic)	Spolic Technosol (Orthothionic, Skeletic)	Typic Udorthent	Sulfic Udorthent
W2	Spolic Technosol	Spolic Technosol (Thionic)	Typic Udorthent	Sulfic Udorthent

diagnostic criteria of *thionic* horizon in WRB (IUSS, 2006) should be supplemented with a remark that macroscopically and microscopically recognizable sulphide minerals, or sulphides recognized using any field test, may occur in *thionic* horizons. Such remark could also be added to the definition of *sulfuric* horizon in the Soil Taxonomy (Soil Survey Staff, 1999). Moreover, it seems justified to add a remark saying that *thionic* horizon may occur not only in soils developed on coastal *sulphidic* materials, but also in technogenic soils developed on mine spoils containing sulphides. A similar remark could be added to the definition of *sulfuric* horizon in the Soil Taxonomy. The approval of the above mentioned remarks would also require supplementing the definitions of *sulphidic* (WRB) and *sulfidic* (Soil Taxonomy) materials, regarding parent technogenic materials (e.g. mine spoils, sludges) containing sulphides as *sulphidic* (*sulfidic*) material. Such materials are currently defined as waterlogged deposits containing sulphides, most commonly occurring in coastal regions. It is also suggested to add the “Thionic” suffix qualifier to the key to the Technosols within the WRB classification (Table 5). It would allow for a better determination of soil properties, and a more precise indication of such properties in names of soils.

Certain problems were encountered when attempting to classify the soils studied according to the criteria given by the Soil Taxonomy (Soil Survey Staff, 1999). On the basis of the soil profile development, the examined soils may be defined as *Entisols*, as they show little or no evidence of the development of pedogenic horizons. Within that Order, the soils studied may be assigned to *Udorthents* Great Group, because they are developed on recent erosional surfaces which are superficial parts of the dumps, and because they are characterized by udic moisture regime. It was hard to assign the soils studied to any of the Subgroup qualifiers specified in the Soil Taxonomy typical of *Udorthents* (Lithic, Vitrandic, Aquic, Oxyaquic, Vermic, and Typic) based on the determined features of the soils (Table 2). Ultimately, they were classified as *Typic Udorthents*. Because of the presence of sulphides and products of their weathering, the use of the adjective “sulfic” would be more relevant. The authors suggest that the *Udorthents* Great Group should be supplemented by the name “*Sulfic*”, which would allow the formation of *Sulfic Udorthents* taxon (Table 5). Weakly developed technogenic soils occurring on mine spoils containing sulphide minerals could be classified under this taxon. The presence of *sulfuric* horizon defined according to the current definition, alternately supplemented in accordance with the above mentioned suggestions, could be the diagnostic soil characteristic of *Sulfic Udorthents*.

4. Conclusions

1. The investigated soils developed on mine spoils containing iron sulphides, regardless of the age, were weakly developed technogenic soils classified as *Spolic Technosols* according to the WRB criteria. The most evident soil-forming process was the accumulation of soil organic matter with age and progressive overgrowing of the mine spoils. An important process changing the properties of soils was the intense weathering of soil material containing sulphides.
2. Along with the proceeding age of soils, the degree of sulphide transformations increased. In the very weakly developed (young) technogenic soils from Trzebinia and Rudki, sulphides were poorly weathered, unlike better developed (older) soils formed in Wiesciszowice, where sulphide minerals were almost entirely transformed into iron oxides and sulphates. In the most acidic soils, amorphous Al-containing iron oxides develop.
3. The Fe_{dith}/Fe_{ox} ratio seems to be a good indicator of the advancement of weathering (soil-forming) processes occurring in technogenic soils developed on mine spoils containing iron sulphides in case where the parent material contain no or very little inherited iron oxides (e.g. goethite) and the main source of “free” Fe in soils are oxidized iron sulphides. The higher the Fe_{dith}/Fe_{ox} ratio, the more advanced weathering and soil-forming processes.
4. Sulphate ions, which were products of sulphide weathering, crystallized as sulphate minerals represented mainly by gypsum and jarosite group minerals. Gypsum developed independently from the soil pH, and jarosite occurred exclusively in acid soils.
5. In acid technogenic soils, intense layer silicate transformations and the formation of swelling clay minerals were determined. Smectite occurring as a discrete or mixed-layer mineral was the main pedogenic phase. Vermiculite also formed. In certain horizons with pH 4.3–4.4, conditions favourable for the development of hydroxy-interlayers within swelling clay minerals occurred.
6. The formation of smectite and vermiculite in the acidic range of pH seems to be dependent on the degree of acidification. Vermiculite forms in less acidic conditions (pH around 4.3–4.4), whereas smectite forms both in less acidic and extremely acid ($pH<3$) soil horizons.
7. On the basis of the soil features presented herein, the paper suggests certain solutions concerning supplementing the *thionic* (WRB) and *sulfuric* (Soil Taxonomy) horizon definitions, as well as the definition of *sulphidic* (*sulfidic*) material. It suggests the introduction of *Sulfic Udorthents* taxon in the Soil Taxonomy, as well as the introduction of “Thionic” suffix qualifier to the key to the *Technosols* (WRB).

Acknowledgments

The investigation was supported financially by the Polish Ministry of Science and Higher Education, grant no. N N305 3251 33. The author would like to thank Mrs. Anna Łatkiewicz, MSc. from the Institute of Geological Sciences of the Jagiellonian University, Krakow, Poland for technical assistance in the mineralogical research. Mr. Wiesław Knap, MSc. is acknowledged for the analysis of extracts from soils. Dr hab. Paweł Bylina (Warsaw University of Technology, Poland), Dr Michał Skiba (Jagiellonian University, Krakow, Poland), Dr Marcin Żyła (Jagiellonian University, Krakow, Poland), Prof. Michael J. Vepraskas (Editor), and two anonymous reviewers are acknowledged for their helpful suggestions which improved the previous draft of the paper. Mrs. Małgorzata Kornijów improved the English.

References

Aoudjit, H., Elsass, F., Righi, D., Robert, M., 1996. Mica weathering in acidic soils by analytical electron microscopy. Clay Miner. 31, 319–332.
April, R.H., Keller, D., Driscoll, T., 2004. Smectite in Spodosols from the Adirondack Mountains of New York. Clay Miner. 39, 99–113.

Bain, D.C., Mellor, A., Wilson, M.J., 1990. Nature and origin of an aluminous vermiculitic weathering product in acid soils from upland catchments in Scotland. Clay Miner. 25, 467–475.

Barnhisel, R.I., Bertsch, P.M., 1989. Chlorites and hydroxy-interlayered vermiculite and smectite. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments. SSSA, Madison, WI, pp. 729–788.

Barnhisel, R.I., Massey, H.F., 1969. Chemical, mineralogical and physical properties of Eastern Kentucky acid-forming coal spoil materials. Soil Sci. 108, 367–372.

Barnhisel, R.I., Rotromel, A.L., 1974. Weathering of clay minerals by simulated acid coal spoil-bank solutions. Soil Sci. 118, 22–27.

Basciano, L.C., Peterson, R.C., 2007. Jarosite–hydronium jarosite solid-solution series with full iron site occupancy: mineralogy and crystal chemistry. Am. Mineral 92, 1464–1473.

Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., Wolf, M., 1996. Schwertmannite and the chemical modeling of iron in acid sulphate waters. Geochim. Cosmochim. Acta 60, 2111–2121.

Bolan, N.S., Curtin, D., Adriano, D.C., 2005. Acidity. In: Hillel, D. (Ed.), Encyclopedia of Soils in the Environment. Elsevier, pp. 11–17.

Borchardt, G., 1989. Smectites. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments. SSSA, Madison, WI, pp. 675–727.

Brindley, G.W., Brown, G., 1980. Crystal Structures of Clay Minerals and Their X-ray Identification. Mineralogical Society, Monograph no. 5, London.

Burlak, T., Alpers, C.N., Foster, A.L., Brown, A., Hammersley, L.C., Petersen, E., 2010. Tracking the Mineralogical Fate of Arsenic in Weathered Sulfides from the Empire Mine Gold–Quartz Vein Deposit by using Microbeam Analytical Techniques. Abstract V51C-2220 presented at 2010 Fall Meeting. AGU, San Francisco, Calif. 13–17 December.

Bzowski, Z., Strzyszcz, Z., 1993. Changes of mineral composition of carboniferous claystones located on hard-coal heaps caused by the weathering processes. Proc. of the 4th Int. Symp. on the Reclamation, Treatment and Utilization of Coal Mining Wastes, pp. 95–99. Krakow, Poland.

Carnicelli, S., Mirabella, A., Cecchini, G., Sanesi, G., 1997. Weathering of chlorite to a low-charge expandable mineral in a Spodosol on the Apennine Mountains Italy. Clays Clay Miner. 45, 28–41.

Cornell, R.M., Schwertmann, U., 2003. The iron oxides: structure, properties, reactions, occurrences and uses, 2nd Edition. Wiley-VCH GmbH & Co, KGaA.

De Kimpe, C., Miles, N., 1992. Formation of swelling clay minerals by sulfide oxidation in some metamorphic rocks and related soils of Ontario Canada. Can. J. Soil Sci. 72, 263–270.

Dixon, J.B., Hosser, L.R., Senkayi, A.L., Egashira, K., 1982. Mineralogical properties of lignite overburden as they relate to mine spoil reclamation. In: Kittrick, J.A., Fanning, D.S., Hossner, L.R. (Eds.), Acid Sulfate Weathering. SSSA Special Publication, Madison, Wisconsin, pp. 169–191. no. 10.

Doner, H.E., Lynn, W.C., 1989. Carbonate, halide, sulfate, and sulfide minerals. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments. SSSA, Madison, WI, pp. 279–330.

Douglas, L.A., 1989. Vermiculites. In: Dixon, J.B., Weed, S.B. (Eds.), Minerals in Soil Environments. SSSA, Madison, WI, pp. 635–674.

Dubiková, M., Cambier, P., Šucha, V., Čaplovičová, M., 2002. Experimental soil acidification. Appl. Geochem. 17, 245–257.

Fanning, D.S., Rabenhorst, M.C., Bigham, J.M., 1993. Colors of acid sulfate soils. In: Bigham, J.M., Ciolkosz, E.J. (Eds.), Soil Color. SSSA Special Publications Number 31, Madison, WI, pp. 91–108.

Fanning, D.S., Rabenhorst, M.C., Burch, S.N., Islam, K.R., Tangren, S.A., 2002. Sulfides and sulfates. In: Dixon, J.B., Schulze, D.G. (Eds.), Soil Mineralogy with Environmental Applications. SSSA, Madison, pp. 229–260.

Galan, E., Carretero, M.I., Fernandez-Caliani, J.C., 1999. Effect of acid mine drainage on clay minerals suspended in the Tinto River (Río Tinto, Spain) An experimental approach. Clay Miner. 34, 99–108.

Grube JR., W.E., Smith, R.M., Ammons, J.T., 1982. Mineralogical alterations that affect pedogenesis in mine soils from bituminous coal overburdens. In: Kittrick, J.A., Fanning, D.S., Hossner, L.R. (Eds.), Acid Sulfate Weathering. SSSA Special Publication, Madison, Wisconsin, pp. 209–223. no. 10.

Hita, R., Torrent, J., 2005. Weathering of pyrite and sphalerite in soils contaminated with pyritic sludge. Soil Sci. Soc. Am. J. 69, 1314–1319.

IUSS Working Group WRB, 2006. World Reference Base for Soil Resources, World Soil Resources Reports No. 103, 2nd edition. FAO, Rome, p. 128.

Jackson, M.L., 1975. Soil Chemical Analysis—Advanced Course. Published by the author, Madison, WI.

Jennings, S.R., Dollhopf, D.J., Inskeep, W.P., 2000. Acid production from sulfide minerals using hydrogen peroxide weathering. Appl. Geochem. 15, 235–243.

Johnson, D.B., 2003. Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines. Water Air Soil Pollut. 3, 47–66.

Kostenko, I.V., Opanasenko, N.E., 2005. Soil formation on sulfide mine dumps in the Western Donets Basin upon their overgrowing. Pochvovedene 11, 1357–1365 in Russian, with English abstract.

Krzaklewski, W., 1990. Analiza działalności rekultywacyjnej na terenach pogórniczych w głównych gałęziach przemysłu wydobywczego w Polsce. Wyd. SGGW–AR, Warszawa. in Polish.

Kubisz, J., 1970. Studies on synthetic alkali-hydronium jarosites I. Synthesis of jarosite and natrojarosite. Miner. Pol. 1, 47–59.

Lagaly, G., Ogawa, M., Dékány, I., 2006. Clay mineral organic interactions. In: Bergaya, F., Theng, B., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier, pp. 309–377.

Lintnerová, O., Šucha, V., Streško, V., 1999. Mineralogy and geochemistry of acid mine Fe-precipitates from the main Slovak mining regions. Geol. Carpathica 50, 395–404.

Loeppert, R.H., Inskeep, W.P., 1996. Iron. In: Sparks, D.L., et al. (Ed.), Methods of Soil Analysis, Part 3. Chemical Methods, SSSA Book Series no. 5, pp. 639–664.

Lu, L., Wang, R., Chen, F., Xue, J., Zhang, P., Lu, J., 2005. Element mobility during pyrite weathering: implications for acid and heavy metal pollution at mining-impacted sites. Environ. Geol. 49, 82–89.

Martín, F., García, I., Díez, M., Sierra, M., Simon, M., Dorronsoro, C., 2008. Soil alteration by continued oxidation of pyrite tailings. Appl. Geochem. 23, 1152–1165.

McDaniel, P.A., Falen, A.L., Tice, K.R., Graham, R.C., Fendorf, S.E., 1995. Beidellite in E horizons of Northern Idaho Spodosols formed in volcanic ash. Clays Clay Miner. 43, 525–532.

Mees, F., Stoops, G., 2010. Sulphidic and sulphuric materials, In: Stoops, G., Marcelino, V., Mees, F. (Eds.), Interpretation of Micromorphological Features of Soils and Regoliths, First edition. Elsevier, pp. 543–568.

Mehra, O.P., Jackson, M.L., 1960. Iron oxide removal from soils and clays by dithionite–citrate system buffered with sodium bicarbonate. Clays Clay Miner., 7th National Conference. Pergamon Press, pp. 317–327.

Moore, D.M., Reynolds, R.C., 1997. X-ray Diffraction and the Identification and Analysis of Clay Minerals. Oxford University Press, New York.

Murad, E., Rojík, P., 2003. Iron-rich precipitates in a mine drainage environment: influence of pH on mineralogy. Am. Mineral. 88, 1915–1918.

Mystkowski, K., 1999. ClayLab, a computer program for processing and interpretation of X-ray diffractograms of clays. Conference of European Clay Groups Association, EUROCLAY 1999, pp. 114–115. Krakow, Poland.

Parafiniuk, J., 1991. Fibroferrite, slavikite and pickeringite from the oxidation zone of pyrite-bearing schists in Wieściszowice (Lower Silesia). Miner. Pol. 22, 3–16.

Parafiniuk, J., 1996. Sulfate minerals and their origin in the weathering zone of the pyrite-bearing schists at Wieściszowice (Rudawy Janowickie Mts., Western Sudetes). Acta Geol. Pol. 46, 353–414.

Parafiniuk, J., Siuda, R., 2006. Schwertmannite precipitated from acid mine drainage in the Western Sudetes (SW Poland) and its arsenate sorption capacity. Geol. Quart. 50, 474–486.

Parfitt, R.L., Henmi, T., 1982. Comparison of an oxalate-extraction method and an infrared spectroscopic method for determining allophane in soil clays. Soil Sci. Plant Nutr. 28, 183–190.

Parker, D.R., 2005. Aluminum speciation. In: Hillel, D. (Ed.), Encyclopedia of Soils in the Environment. Elsevier, pp. 50–56.

Poch, R.M., Thomas, B.P., Fitzpatrick, R.W., Merry, R.H., 2009. Micromorphological evidence for mineral weathering pathways in coastal acid sulfate soil sequence with Mediterranean-type climate South Australia. Aust. J. Soil Res. 47, 403–422.

Pracz, J., Kwasowski, W., 2001. Charakterystyka kwaśnych gleb siarczanowych występujących w rejonie Mrzeżyna. Rocz. Glebozn. 52, 23–37 in Polish, with English abstract.

Reid-Soukup, D.A., Ulery, A.L., 2002. Smectites. In: Dixon, J.B., Schulze, D.G. (Eds.), Soil Mineralogy with Environmental Applications. SSSA, Madison, WI, pp. 467–499.

Righi, D., Räisänen, M.L., Gillot, F., 1997. Clay mineral transformations in podzolized tills in central Finland. Clay Miner. 32, 531–544.

Ritsema, C.J., van Mensvoort, M.E.F., Dent, D.L., Tan, Y., van den Bosch, H., van Wijk, A.L.M., 2000. Acid sulfate soils. In: Sumner, M.E. (Ed.), Handbook of Soil Science, pp. G-121–G-154.

Ross, G.J., Wang, C., Ozkan, A.I., Rees, H.W., 1982. Weathering of chlorite and mica in a New Brunswick podzols developed on till derived from chlorite-mica schist. Geoderma 27, 255–267.

Ross, G.J., Eilers, R.G., Ivarson, K.C., 1988. Influence of acid sulfate weathering on chemical and mineralogical properties of an acid sulfate soil of Manitoba. Can. J. Soil Sci. 68, 629–644.

Schwertmann, U., 2008. Iron oxides. In: Chesworth, W. (Ed.), Encyclopedia of Soil Science, pp. 363–369.

Singh, B., Wilson, M.J., McHardy, W.J., Fraser, A.R., Merrington, G., 1999. Mineralogy and geochemistry of ochre sediments from acid mine drainage near a disused mine in Cornwall UK. Clay Miner. 34, 301–317.

Siuta, J., Rejman-Czajkowska, M., 1980. Siarka w biosferze. PWRiL, Warszawa. in Polish.

Skawina, T., 1959a. Procesy zniekształcania gleb w okręgach górniczych i przemysłowych. Rocz. Glebozn. 7, 131–148 in Polish, with English abstract.

Skawina, T., 1959b. Przebieg rozwoju procesów glebotwórczych na zwałach kopalnictwa węglowego. Rocz. Glebozn. 7, 149–162 in Polish, with English abstract.

Skawina, T., Trafas, M., Gołda, T., 1974. Rekultywacja terenów pogórniczych kopalni pirytu „Siarkopol" w Rudkach k. Kielc. Zeszyty Naukowe AGH, no. 466. Sozologia Sozotechnika 4, 9–21 in Polish, with English abstract.

Skiba, M., 2007. Clay mineral formation during podzolization in an alpine environment of the Tatra Mountains Poland. Clays Clay Miner. 35, 618–634.

Smith, J., Melville, M.D., 2004. Iron monosulfide formation and oxidation in drain-bottom sediments of an acid sulfate soil environment. Appl. Geochem. 19, 1837–1853.

Soil Survey Staff, 1999. Soil Taxonomy. Agriculture Handbook no. 436, USDA.

Šourková, M., Frouz, J., Šantrůčková, H., 2005. Accumulation of carbon, nitrogen and phosphorus during soil formation on alder heaps after brown-coal mining, near Sokolov (Czech Republic). Geoderma 124, 203–214.

Środoń, J., 2006. Identification and quantitative analysis of clay minerals. In: Bergaya, F., Theng, B., Lagaly, G. (Eds.), Handbook of Clay Science. Elsevier, pp. 765–787.

Struthers, P.H., 1964. Chemical weathering of strip-mine spoils. Ohio J. Soil Sci. 64, 125–131.

Strzyszcz, Z., 1978. Chemiczne przemiany utworów karbońskich w aspekcie biologicznej rekultywacji i zagospodarowania centralnych zwałowisk. Prace Studia PAN 19 in Polish, with English summary.

Strzyszcz, Z., 1989. Ocena przydatności odpadów górniczych Górnośląskiego Zagłębia Węglowego do rekultywacji biologicznej. Arch. Ochr. Środ. 1–2, 91–123 in Polish, with English abstract.

Šucha, V., Dubiková, M., Cambier, P., Elsass, F., Pernes, M., 2002. Effect of acid mine drainage on the mineralogy of a dystric cambisol. Geoderma 110, 151–167.

Thomas, D., Jansen, I., 1985. Soil development in coal mine spoils. J. Soil Water Conserv. 40, 439–442.

Twardowska, I., Szczepańska, J., Witczak, S., 1988. Wpływ odpadów górnictwa węgla kamiennego na środowisko wodne. Ocena zagrożenia, prognozowanie, zapobieganie. Prace studia PAN 35 in Polish, with English abstract.

Uzarowicz, Ł., 2011. Technogenic soils developed on mine spoils containing iron sulfides in selected Polish abandoned industrial sites: environmental hazards and reclamation possibilities. Polish J. Environ. Stud 20, 137–148.

Uzarowicz, Ł., Skiba, S., Skiba, M., Michalik, M., 2008. Mineral transformations in soils on spoil heaps of an abandoned pyrite mine in Wieściszowice (Rudawy Janowickie Mts., Lower Silesia, Poland). Polish J. Soil Sci. 41, 183–193.

van Reeuwijk, L.P., 2002. Procedures for soil analysis. Technical Paper 9. ISRIC, Wageningen.

Wagner, D.P., Fanning, D.S., Foss, J.E., Patterson, M.S., Snow, P.A., 1982. Morphological and mineralogical features related to sulfide oxidation under natural and disturbed land surfaces in Maryland. In: Kittrick, J.A., Fanning, D.S., Hossner, L.R. (Eds.), Acid Sulfate Weathering. SSSA Special Publication, Madison, Wisconsin, pp. 109–125. no. 10.

Wieser, T., 1949. Siarczanowe produkty wietrzenia na złożu dwusiarczku żelaza Gór Świętokrzyskich. Roczn. Pol. Tow. Geol. 19, 445–477 in Polish, with English abstract.

Wójcik, J., Krzaklewski, W., 2007. Akumulacja materii organicznej w inicjalnych glebach na zwałowisku zewnętrznym Kopalni Węgla Brunatnego "Adamów". Rocz. Glebozn. 58, 151–159 in Polish, with English abstract.