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Original Research

Mineralogical Alterations of Zn-Pb Flotation Wastes of Mississippi Valley-Type Ores (Southern Poland) and Their Impact on Contamination of Rainwater Runoff

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Abstract

Research was carried out on the slopes of a tailings pond built from carbonate wastes, rich in metal flotation wastes of Mississipi Valley-Type Zn-Pb ores in the Silesia-Kraków ore district (southern Poland). These wastes, resulting from Zn-Pb ore processing, may have a detrimental impact on the environment. This study presents results of chemical (ICP, IC, AAS) and mineralogical (XRD, SEM-EDS) characterizations of material from the superficial waste layer, water runoff and relocated suspension. They indicate the occurrence of several secondary mineral phases (Fe oxide, Zn and Pb carbonate, and sulfate-containing metals), resulting from the weathering processes of primary Fe, Zn, and Pb sulfides. Results of XRD and SEM examinations point to the increase of sulfate mineral content in the top layer of wastes compared to the wastes in depth. Rainwater runoff (RWR) on the slopes of tailings is characterised by the prevalence of calcium and sulfate, as well as the presence of metals such as Zn, Fe, Mn, Sr and Cd. Metals and sulfates migration in RWR is one of the ways of contaminants' spreading around Zn-Pb processing mine tailings.

Keywords: rain water runoff, flotation waste, heavy metals, secondary mineral phases

Introduction

The environmental impact of polymetallic ore flotation in waste dumps results mainly from heavy metals (HM) and sulfate transfer. The effect of post-processing metalliferous wastes on air, soil, water and living organism contamination is significant and is the subject of geochemical [12, 14, 26, 28, 29], toxicological [13, 20, 25] and biological research [36]. Tailing ponds covering an area of over 100 or even 1,000 hectares are placed in the vicinity of mines exploiting Cu (kuperschiefer and porphyry types) and Zn-Pb (sedimentary-exhalative-SEDEX, Mississippi Valley Type-MVT and supergene-type) deposits. Their influence becomes significant in larger areas as a result of fine-grained fractions rich in heavy metals transported to top soil by wind [5]. The heavy metals concentrations associated with easily leachable fractions are transferred to surface and ground waters [8]. Contamination of water environment is commonly connected to the well known processes of weathering and leaching of metalliferous wastes as a result of typical acid mine drainage (AMD) [32, 33] from wastes poor in carbonates.

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In regions of metal mining and non-ferrous metallurgy, rainwater runoff (RWR) processes seem to have a significant influence on the ability of metals to migrate. Their environmental significance in the abandoned Wemyss mining area (western Wales) was suggested by Merrington and Alloway [24]. Studies conducted on the ponds of the Trojan Nickel Mine (Zimbabwe) showed high concentrations of sulfate (over 100 mg L^{-1}), as well as Pb (> 1.0 mg L^{-1}) and Ni (> 0.2 mg L^{-1}) in water of pH 7.0-8.5 [21]. Leaching of heavy metals during heavy rains may influence overall balance of water and soil contamination. Incidental heavy rains and rain erosion of wastes may lead to the release of significant quantities of Pb, Zn and Cd, reaching even hundreds of kilograms annually. These processes are of long-term character, and even several years after mining activity, large amounts of HM are still being released to the environment [13, 24]. Studies conducted in the USA [16, 17] show evaporative crystallization of sulfate minerals to play an important role in heavy metals migration in a moderate climate zone. Fe, Al, Ca and Mg sulfates were found by Keith et al. (2001) in Iron Mountain (California) [17]. Over 40 easily leachable sulfate minerals of Fe, Al, Ca, and Mg, and additionally Zn, Pb and Cu were described by Hammarstrom et al. (2005) from the eastern ore areas of the USA [16]. Their occurrence was linked to weathering of massive sulfide deposits.

The environmental impact of waste dumps from Zn-Pb MVT ore processing is poorly known [9], particularly in relation to the heavy metal and sulfates potential which can be transferred to waters, soils and trophic chains. Among all processes affecting environmental contamination impact in the regions of mining and metal ore processing (eolian wastes transport, leachate infiltration, surface runoff), RWR is not sufficiently known. This investigation aims at the study of secondary geochemical changes in the top layer of carbonate wastes, resulting from Zn-Pb ores of MVT flotation, as well as preliminary evaluation of the phenomenon scale and RWR role in the HM and sulfate leaching processes.

Study Area

Research was carried out on over-the-level tailings ponds built of post-flotation wastes (Fig. 1) that have been deposited from 1968. They are located close to Olkusz (50°16'32"N and 19°30'00"E) in southern Poland. The tailings ponds hosted over 60 M tones of fine-grained waste material (over 88% by weight comprises fraction from 0.025 to 0.2 mm) [15]. They cover an area of 110 hectares and their height reaches 42 m over the land surface.

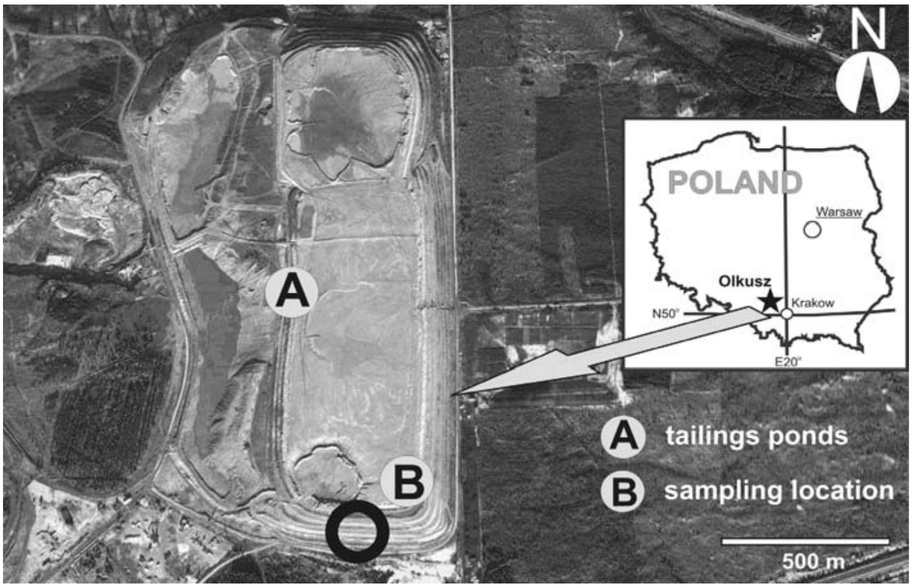

Fig. 1. Location of study area.

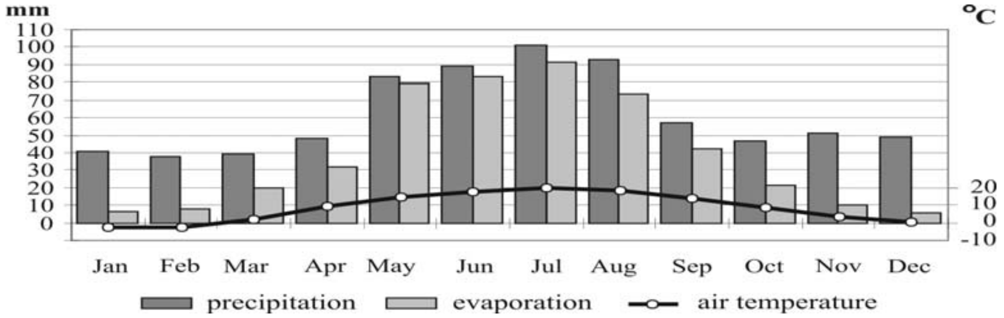

Fig. 2. Monthly average values of precipitation, air temperature and evaporation in the study area from 2003 to 2007.

Weather Condition

Tailings ponds are located in the moderate climate zone ca. 320 m above sea level. Average annual air temperature is 7.1°C. Annual precipitation from 1961-1990 was 736 mm [30]. The highest values of precipitation occurred in the period from May to August, when an abundant stormy rainfall occurs. In the study area, the precipitation is higher than evaporation, which is 472 mm annually [31] (Fig. 2).

Geological Setting of Zn-Pb Deposits

Silesia-Kraków deposits of Zn-Pb ores occur in epigenetic, ore-bearing dolomites accumulating in paleosome of calcereous mid Triassic, and are categorized as MVT formation deposits. These deposits include as main constituents sphalerite (α ZnS), wurtzite (β ZnS) and galena (PbS) [34]. In the primary mineralization, polymorphic forms of Fe sulfides (FeS_2) also occur (markasite and pyrite are most abundant) [2]. In association with main Zn-Pb-Fe sulfides, barite ($BaSO_4$) as well as trace quantities of greenockite (CdS) and sulfosalts As-Pb are present. Some parts of deposits close to the surface were oxidized, representing a supergene environment. In this oxidized zone the mineral composition includes smithsonite ($ZnCO_3$), cerussite ($PbCO_3$), goethite (α FeO(OH)) and lepidocrocite β FeO(OH), Mn oxides of Ca, Mg, Fe, Zn, Pb [3, 19, 34, 37]. For the primary Zn-Pb-Fe sulfides in Silesia-Cracow deposits typical chemical elements are: Cd, Tl, Mn, As, Ag, Co, Ge, In, Se [1, 22, 23].

Methods

Field Experiment

A part of the southern slope of the tailings pond was equipped with a system of five 2-meter gutters for collection of RWR samples. The gutters formed 5 study polygons (P1, P2, P3, P4 and P5) collecting RWR from the surface of 60 m^2 (Fig. 3).

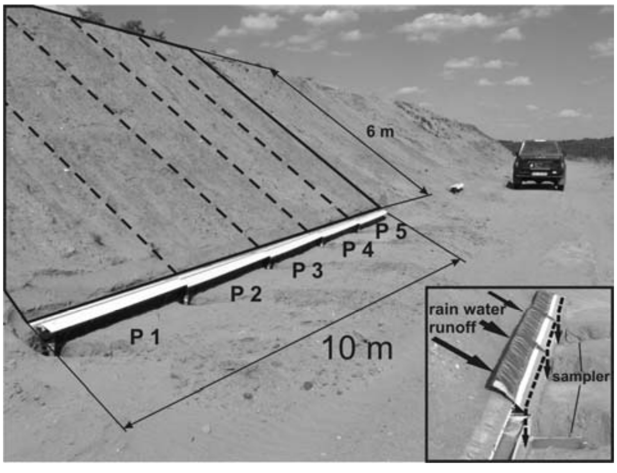

Fig. 3. Slope of tailings pond with polygons and gutters designed for RWR sampling.

The gutters were designed to retain water and suspensions flowing down the slope, but not the water falling directly from precipitation. RWR and suspensions samples were taken in early September 2007, instantly after an intense rain (26.5 mm within 350 minutes) – which resulted in the formation of runoff and waste erosion. The sampling of RWR was at the end of a five day period of rain.

Methods

Water samples were collected polyethylene bottles 0.5 l each. Measurements of pH and electric conductivity (EC) were performed in the field using a WTW MultiLine P4 integrated meter. Ion chromatography (IC) tests (Dionex, ICS-2500) were used to determine Cl- and SO_4^{2-} anion constituents of waters, and HCO_3^- was analyzed by titration (uncertainty of methods for main ions varied from 2 to 3%). Inductively coupled plasma atomic emission spectrometry (ICP-AES) (PerkinElmer, Optima™ 3000 DV) was used to determine Ca, Mg, Na, K, Si, As, Ba, Cd, Cr, Cu, Ni, Pb, Sr, and Zn (uncertainty 5%). Mineral composition was determined by X-ray diffraction (Philips PW 3720 X-ray difractometer). Scanning electron microscopy (SEM) (Philips, XL 30 ESEM/TMP) with energy dispersive spectrometry (EDS) were used for examination of mineral composition of wastes from outer parts of the tailings pond and selected suspensions. In the RWR samples, contents of total dissolved solids (TDS) were additionally determined. Water analyses were performed on the samples filtered through a 0.45 μm membrane filter. Suspensions retained by the filter were dried at 105ºC and then digested in aqua regia. Tests were performed in the laboratories of the Department of Environmental Monitoring in the Central Mining Institute in Katowice and Faculty of Earth Sciences in the University of Silesia in Sosnowiec.

Results and Discussion

Mineral Composition of Wastes

The postflotation wastes from Zn-Pb ore processing are dominated by carbonates (dolomite, calcite, ankerite) and aluminosilicates, whose overall participation is about 80% (Fig. 4). However, the share of sulfides as well as oxidized Zn, Pb and Fe minerals is very high and reaches 20% by weight [2, 15]. Fe sulfides prevail among metalliferous minerals. The amount of Fe sulfides in wastes deposited in various periods of time was changing from 11 do 17% by weight [4]. Participation of Zn-bearing minerals (sphalerite and smithsonite) in wastes reaches 1.9% by weight, whereas lead-bearing minerals – mainly galena and cerussite – amount to 0.8% by weight [15]. The significance of galena's initial presence ~0.5% in wastes was underlined by Kucha and Jędrzejczyk [18]. Total content of Ag, As, Ba, Cd, Co, Cr, Cu, Ni, Sr and Tl in wastes does not exceed 0.1% by weight [2, 15].

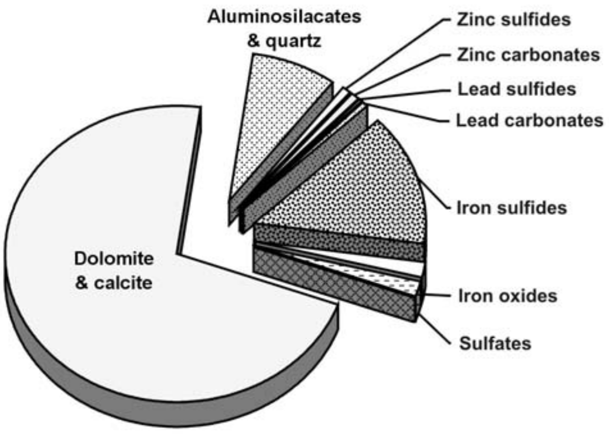

Fig. 4. Average mineral composition of flotation wastes from tailing ponds in Olkusz ore district [5].

The SEM investigation of the wastes exposed on the surface indicates that their mineral composition is different relative to wastes from deeper layers of the pond. The semi quantitative mineral content of the superficial layer obtained by the interpretation of XRD data is given in Table 1.

SEM investigations showed the Fe, Zn, and Pb sulfides to be of fine grain size from 0.1 to 150 µm (Fig. 5a). The seldom observed galena grains were markedly dissolved and frequently covered with coats of submicroscopic thickness (0.1-1µm) made from hydrated Fe sulfates (Fig. 5b) of diversified composition (Table 1). Processes of secondary crystallization lead to the formation of polymineral aggregates composed of sulfates and carbonates. Significant secondary alterations were observed mainly on large galena grains (>100 µm) (Fig. 5e) of oval shape and whose surface was often covered by Pb carbonate (cerussite).

Galena oxidizes much faster than other sulfides and its abundance is known to decrease significantly during the first 20-40 years after exposure to a tailing environment [29]. In the conditions of high carbonate content, cerussite is the main product of galena oxidation. Cerussite is a stable mineral in the oxidative surface environment and is practically insoluble in neutral pH water ($K_{sp}= 3.30\times10^{-14}$) [29]. Grain size of the cerussite recorded in the superficial waste layer ranged from 2 to 30 µm in diameter. Most of the grains had tabular morphology with rounded edges and represented partially a primary ore mineral (Fig. 5f).

Examination under the SEM-EDX enabled us to identify other rare, secondary lead minerals: phosphates (pyromorphite), chlorides and vanadates (Fig. 5g), present in the samples in trace amounts. Precipitation of lead chloride (probably cotunnite) requires an acidic environment and high chloride activities [10]. Lead chloride was found to precipitate on pyrite surfaces (Fig. 5h). Skeletal crystals of sylvine (KCl) growing on sphalerite grain (Fig. 5i) confirmed a locally high chloride activity, probably enhanced in the periods of intense evaporation. The secondary minerals, though small (below 10 µm), lacked any signs of weathering.

Table 1. Mineral composition of the top layer of wastes (semi-quantitative XRD data).

Main gangue components	dolomite $CaMg(CO_3)_2$	+++++
	ankerite $CaFeMg(CO_3)_2$	++
	calcite $CaCO_3$	++
	illite	++
	montmorillonite	+
	kaolinite	+
	quartz SiO_2	+
Sulfides	marcasite FeS_2	++++
	pyrite FeS_2	++
	sphalerite ZnS	+
	galena PbS	+
	greenockite CdS	-
Secondary metalliferous carbonates and silicates	smithsonite $ZnCO_3$	+
	cerussite $PbCO_3$	+
	hemimorfite $Zn_4Si_2O_7(OH)_2$ H_2O	-
Sulfates and oxides	goethite a FeO(OH)	+++
	gypsum $CaSO_4 \cdot 2H_2O$	+++
	anglesite $PbSO_4$	+
	barite $BaSO_4$	+
	Mn oxides	+
	bassanite $CaSO_4 \cdot 0.5H_2O$	-
	jarosite $KFe_3[(OH)_6/(SO_4)_2]$	-
	melanterite $FeSO_4 \cdot 7H_2O$	-
	rozenite $FeSO_4 \cdot 4H_2O$	-
	epsomite $MgSO_4 \cdot 7H_2O$	-
	hexahydrite $(Mg,Zn,Fe)SO_4 \cdot 6H_2O$	-
	boyleite $(Zn,Mg)SO_4 \cdot 4H_2O$	-
	bianchite $(Zn,Fe^{2+})SO_4 \cdot 6H_2O$	-
	copiapite $Fe_5(SO_4)6(OH)_2 \cdot 20H_2$	-

+++++ - dominant component > 50%, ++++ - between 50 and 5%, +++ - 5 and 2%, ++ - 2 and 1%, + - 1 and 0.1%, - trace content.

Defects of the crystal lattice as well as the polymineral character of aggregates promote Zn sulfide oxidation. The sphalerite weathering rate also depends on the solid solution iron content in the sphalerite structure. The rate of dissolution is considerably faster for iron-rich sphalerite [35]. On the other hand, the rate-enhancing effect is hindered by the development of a layer composed of oxidation products [11, 18]. The iron-rich sphalerites were coated or transformed into iron sulfates that contained a varied amount of

Zn in the investigated samples. The formation of secondary sulfate minerals, followed by their dissolution in the changeable surface conditions, is probably the main source of leached heavy metals and one of the main sources of sulfate ions. The grain size of the iron-poor, primary sphalerite was between 10 and 70 µm in diameter. The grain surfaces were porous to a variable extent and no oxidation product coatings were observed on them (Fig. 5i).

The group of secondary sulfate minerals was also represented by diversified unstable Ca, Mg, Fe and Zn sulfates formed as a result of evaporation. The decrease of humidity in wastes caused by the group of sulfate minerals, mainly bassanite, was preserved [6]. White efflorescent salts occurring on tailing surfaces within the investigated polygon were composed of gypsum and, to a lesser degree, of hydrated magnesium sulfates such as epsomite and hexahydrite.

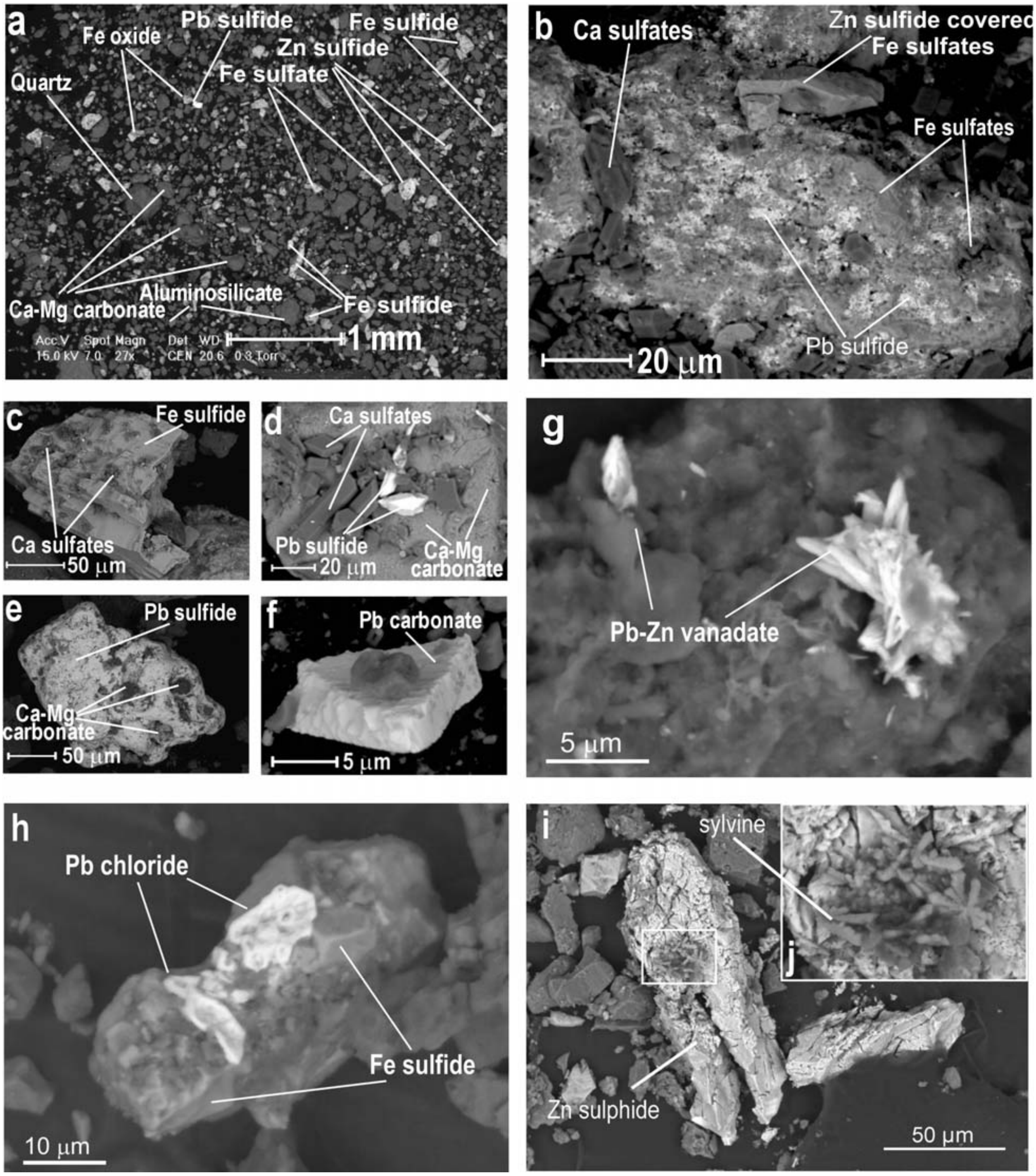

Fig. 5. SEM (BSE) images of minerals from upper layer floatation wastes of Zn-Pb ores. (a) - A general view of a waste sample showing the amount of heavy metal hosting grains (light) relative to gangue minerals. (b, c, d, e, f) - Sulfates and carbonates together with primary ore minerals (galena, Fe sulfide, Zn sulfide) showing different levels of alteration. (g) - A secondary Pb-Zn vanadate. (h) - Fe sulfide partially covered by Pb chloride (probably cotunnite). (i) - Partially dissolved pure Zn sulfide with sylvine crystals. (j) - Part of image (i) enlarged to show the sylvine precipitates.

Table 2. Trace metal concentrations in the runoff suspended fine fraction.

Zn	Pb	As	Ba	Cd	Sr	Cu	Ni	Cr
mg kg^{-1}								
8,555	3,500	456	233	62	63	60	27	17

Cadmium was predominantly connected with zinc sulfides, however at the stage of sulfides weathering, the geochemical split of Zn from Cd is noted, which may result in the formation of Cd minerals such as greenockite (CdS) or otavite ($CdCO_3$) [3]. Manganese was present in relatively stable Fe and Mn (hydro)oxides and was also recorded in organo-metallic phases of soil top layers [5].

The mineral composition of the fine grain fraction suspended in runoff waters was found to be much simplified relative to the wastes. The suspension was composed dominantly of dolomite (50-52%) with lower concentrations of quartz (10-15%) and calcite (10-12%). Clay minerals (~8%) and feldspars (6-8%) were present as minor components. Pyrite and marcasite (10-12%) were the only sulfides detected using XRD. A typical diffraction pattern is shown in Fig. 6.

Minerals hosting metals other than Fe were present in trace amounts and were detected only after applying SEM imaging. Due to its low detection limits ~ 5 wt %, the XRD method did not enable the identification of mineral phases containing such metals as Zn, Pb, Cd, As and others. Their presence, however, was confirmed by indicative ICP-AES analyses (Table 2) and EDS microanalysis of submicroscopic metalliferous grains investigated using SEM.

Galena grains were not found in the suspension. The majority of Pb was present within the cerussite structure. Additionally, Pb was found to be occluded in Fe (hydro)oxides together with Zn in the suspension. The relative abundances of Zn and Pb adsorbed onto the Fe (hydro)oxides were variable. Zinc in the suspension was present mainly within an iron-poor, primary sphalerite. A commonly observed secondary iron sulfate, a weathering product of the iron-rich sphalerite, was also an important zinc-bearing phase. Zn silicate (hemimorphite) was found in trace amounts. Pyrite/marcasite, present in substantial quantities within the fine fraction, was mostly unaltered.

Chemistry of Water Runoff

Rainwater runoff, collected at the base of the investigated slope, had variable pH values. Water samples from polygons P1, P2, and P3 have weak basic pH (ca. 7.3), whereas pH of waters marked P4 and P5 had pH values of 6.8 and 6.0, respectively, corresponding to slightly acidic conditions. Electrical conductivity (EC) of the RWR from polygons P1, P2 and P3 ranged from 387 to 422 µS cm^{-1} and was significantly lower than the values observed for P4 and P5 waters (668 and 757 µS cm^{-1}) (Table 3). Total dissolved solid (TDS) values for P1, P2, and P3 samples was from 295 to 313 mg L^{-1}, while for P3 and P4 they were higher: 549 and 601 mg L^{-1}, respectively.

Differences in the concentration of main ions were observed in the RWR (Table. 3). Waters from polygons P1, P2, and P3 showed Ca^{2+} and SO_4^{2-} concentrations ranging from 84 to 91 mg L^{-1} and from 188 to 199 mg L^{-1}, respectively. Ca^{2+} concentrations for polygon waters P4 and P5 were significantly higher (to 158 and 173 mg L^{-1}, respectively). Concentrations of SO_4^{2-} were 367 and 402 mg L^{-1}, respectively. Similar differences were observed for Mg^{2+} and SiO_3^{2-}. Whereas concentrations of HCO_3^- did not fit to the described pattern and were similar in all samples. Concentrations of Na, Pb and Cu in examined water samples did not exceed detection limits and are not presented in the table.

Among the group of examined metals, the concentrations of Fe_{og}, Mn, Sr, Zn, and Cd followed the changes observed for the main ion concentrations in RWR (Table 3). Zn concentrations for P4 and P5 waters (1.23 to 1.3 mg L^{-1}) were higher than for P1, P2 and P3, which contain from 0.59 to 0.74 mg L^{-1} of Zn. Cadmium concentrations in waters from P1 to P3 were low and remain in the narrow range from 0.018 to 0.02 mg L^{-1}, whereas waters P4 and P5 had higher concentration (up to 0.34 mg L^{-1}).

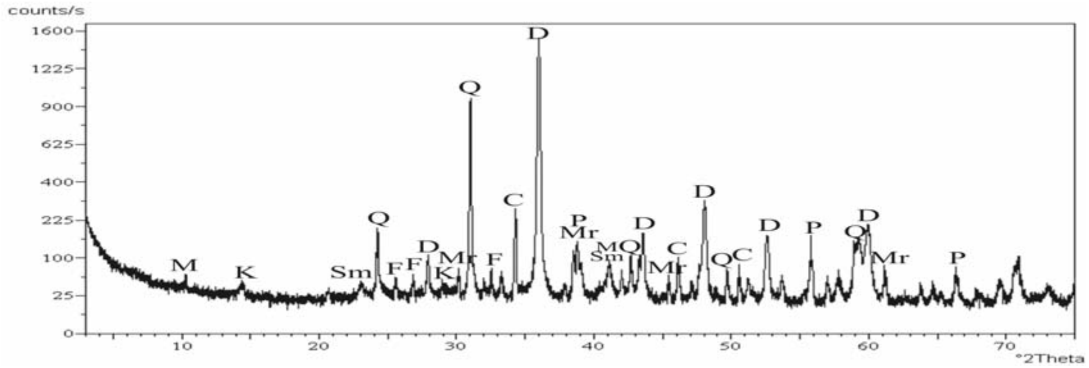

Fig. 6. XRD pattern of suspension sample: C-calcite, D-dolomite, F- feldspars, K-kaolinite, M-muscovite, Mr–marcasite, P–pyrite, Sm–smectite, Q-quartz.

Table 3. Chemical composition of rainwater runoff from carbonate flotation wastes.

	EC	pH	TDS	Ca	Mg	K	Cl^-	SO_4^{2-}	HCO_3^-	SiO_3^{2-}	Fe_{og}	Mn	Sr	Zn	Cd
	µS/cm	-	mg L^{-1}												
P 1	387	7.35	295.0	83.77	1.37	0.203	< 0.3	188.0	33.6	1.08	0.1	0.038	0.045	0.62	0.02
P 2	393	7.3	294.0	83.77	1.43	0.141	< 0.3	189.0	30.5	1.03	0.098	0.044	0.042	0.59	0.018
P 3	422	7.3	313.0	90.58	1.59	0.141	< 0.3	199.0	33.6	1.2	0.12	0.052	0.049	0.74	0.018
P 4	668	6.8	549.0	158.3	1.99	0.094	0.408	367.0	30.5	1.21	0.14	0.08	0.07	1.3	0.034
P 5	757	6.0	601.0	173.3	2.22	0.145	< 0.3	402.0	33.6	1.56	0.15	0.078	0.076	1.23	0.034

The differences in chemical composition between water samples from subsequent polygons are related to supplying surface and residence time of runoff before reaching the gutters. Waters from P1, P2 and P3 polygons showing higher pH and lower main ions and metal concentrations run only off the surface of the studied slope area and from the fragment of the shelf above. Waters coming from the larger surface of the tailings pond slope, collected in gutters P4 and P5, show lower pH and higher sulfides and HM concentrations. Results and field observations point to the correlation of a larger area of runoff and longer residence time of RWR at top layers of wastes with leaching of secondary soluble mineral forms containing calcium, sulfates and metals: Fe, Zn, Mn, Sr, and Cd.

It was shown that pH decreases and TDS increases in investigated RWR and values of electric conductivity (EC) were high, as well as the concentrations of Ca^{2+} and SO_4^{2-} and metals. These observations are consistent with the results obtained by Navarro et al. [27] in the areas of the mining district Cabezo Rajao in SE Spain and Lupankwa et al. [21] from the region of the Trojan Nickel Mine in Zimbabwe. High Ca^{2+} concentration together with relatively high SO_4^{2-} concentration was described in classical AMD environment. The SO_4^{2-} ions, which are produced by the oxidation of sulfides, locally lead to pH decrease and, in this way, promote the dissolution of carbonate minerals [7].

Presented results demonstrate leaching of contaminants from wastes after several days of intense rain. It is assumed that RWR are enriched in Ca^{2+}, SO_4^{2-} and some metals after a prolonged rainless period.

Conclusion

Mineral alterations observed in postflotation tailings ponds built of flotation carbonate wastes of MVT formation lead to the precipitation of secondary soluble mineral phases containing metals. Dissolution of these mineral phases and the migration of Zn, Fe, Mn, Sr and Cd in RWR out of the dump area play an important role in the contamination of the surrounding environment.

In the future, contaminant transfer in RWR may increase as a consequence of confirmed climate changes leading to the intensification of violent atmospheric phenomena. In this case intensification of geochemical changes in wastes followed by the leaching of contaminants by RWR to the environment may occur. This is why studies leading to the better knowledge of the RWR role should be continued, particularly to determine the amounts of HM and sulfate leached by runoff waters produced by increased seasonal precipitation linked to climatic change.

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